

The Journal *of the* SOCIETY OF DYERS AND COLOURISTS

Volume 72 Number 5

CONTENTS

PROCEEDINGS OF THE SOCIETY

- THE CONTROL OF SODIUM HYDROSULPHITE IN
VAT DYEBATHS (W. J. Marshall) 201

COMMUNICATIONS

- THE IDENTIFICATION OF VAT DYES (D. A. Derrett-Smith and J. Gray) 211

- POLAROGRAPHIC INVESTIGATION OF FUR DYES AND
THEIR OXIDATION PRODUCTS (G. Sandberg) 227

- DETECTION OF DYES POSSESSING A β -PHENYLENEDIAMINE
OR A β -NITROANILINE STRUCTURE BY MEANS OF
SPOT TESTS (F. Feigl and C. Costa Neto) 239

- CORRESPONDENCE 241

- NOTES 242

- OBITUARY NOTICES 245

- NEW BOOKS AND PUBLICATIONS 246

- ABSTRACTS 247

THE SOCIETY OF DYERS AND COLOURISTS
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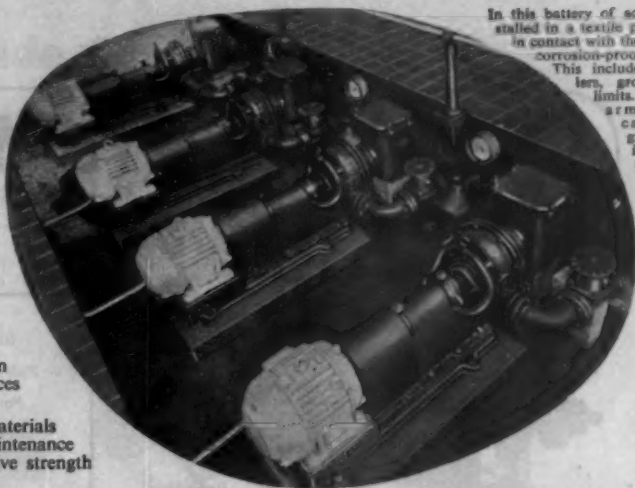
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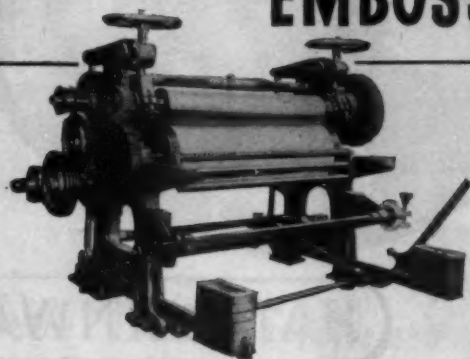
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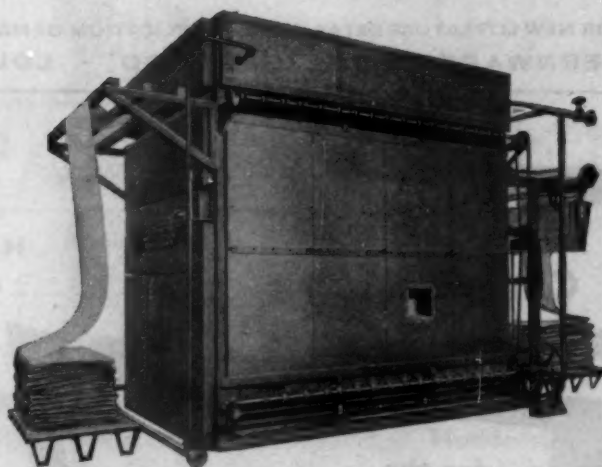
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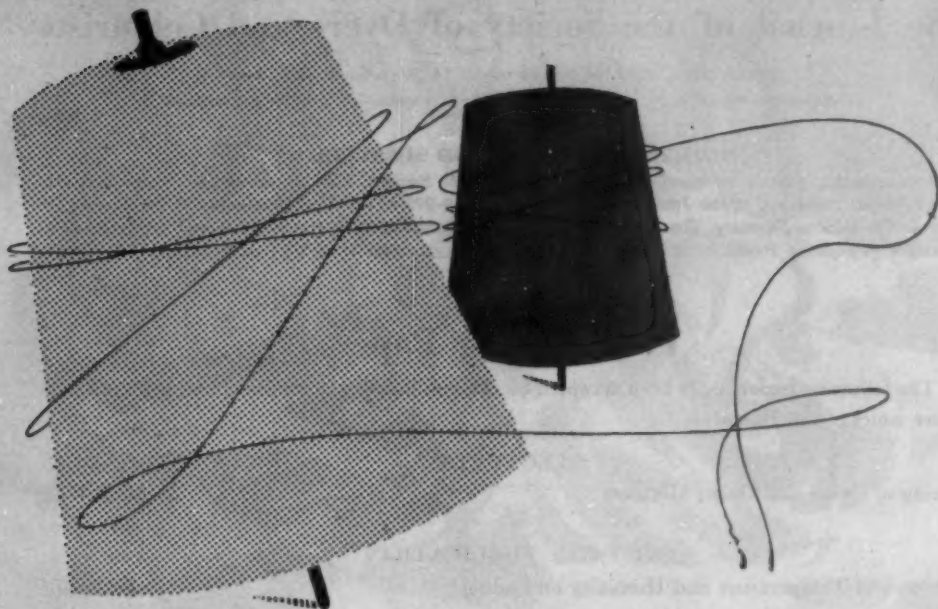
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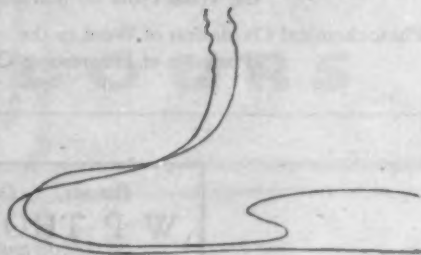
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Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

LECTURES

Dyeing of Orlon and Orlon Mixtures

I. M. S. Walls

F.T.C.C. PUBLICATION

Influence of Temperature and Humidity on Fading

P. W. Cunliffe

COMMUNICATIONS

Package Dyeing—II

W. Armfield, J. Boulton, and J. Crank

Spectrophotometric Studies on Metal-Dye Complexes—I

R. B. Bentley and J. P. Elder

Interaction between Chlorazol Sky Blue FF

and Chrysophenine G in Aqueous Solution *A. N. Derbyshire and R. H. Peters*

Influence of Histological Factors on the Attack of
the Wool Fibre by Various Reagents

R. L. Elliott and J. B. Roberts

Photochemical Oxidation of Wool in the
Presence of Fluorescent Compounds

D. R. Graham and K. W. Statham

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Volume 72 Number 5

MAY 1956

Issued Monthly

Proceedings of the Society

The Control of Sodium Hydrosulphite in Vat Dyebaths

W. J. MARSHALL

One-day Symposium on "Laboratory Control of Dyeing and Finishing Processes" held by the Manchester Section at the Manchester College of Technology on 18th March 1955, Mr. J. Boulton in the chair

In vat dyebaths, the basic information required for control of the hydrosulphite is the rate at which it must be replaced and the properties of the dye which determine the minimum concentration of hydrosulphite necessary for successful dyeing. For this reason the rate of oxidation of hydrosulphite solutions has been measured over a wide range of conditions, and the results have been related to typical practical systems. The reduction properties of vat dyes are discussed with reference to their reduction potentials, and it is shown that electrometric methods can be satisfactorily applied to dyebath control only in special circumstances. The overriding difficulty is the insensitivity of the electrode to changes in hydrosulphite concentration and the variable speed—always low—with which a steady potential is reached. It is concluded that the most satisfactory method of control depends on an initial quantitative study and thorough understanding of the hydrosulphite requirements of the dyeing system. Methods of measuring hydrosulphite concentration suitable for dyehouse use are briefly described.

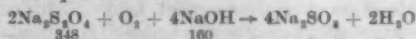
Introduction

It is generally recognised that the highest standard of colour fastness on cotton usually requires the use of vat dyes, and even these do not always give satisfactory results. The application of this class of dye requires not only a larger number of processes but also greater skill and control than are necessary for other dyes; thus, apart from the cost of the dye itself, the process of dyeing is more expensive, so that economy and uniformity are ideals of particular importance. The soluble alkaline leuco (or reduced) form is normally used, but this form is unstable, and it is only by careful control and use of the correct amount of reducing agent that successful dyeings can be made.

If too little reducing agent is used, oxidation occurs and the dye comes out of solution. This results in such faults as poor colour value, incorrect colour, heavy selvages in jig dyeing, and poor fastness to rubbing, to mention only a few. If too much reducing agent is used, expensive chemicals are wasted, excessive time is required for oxidation, particularly in continuous dyeing, and there is the danger of changing the shade or even destroying the dye. The control of hydrosulphite concentration is quite evidently of paramount importance in all methods of dyeing with vat dyes, and to the experienced dyer this does not require emphasis. On the other hand, if too little alkali is used, the dye is precipitated as the insoluble and non-

substantive acid leuco compound. In any of these events a bad dyeing is the result.

Sodium hydrosulphite is the most frequently employed reducing agent in vat dyeing, but it must be realised that in use it gives acid oxidation products, and it is therefore essential always to add a sufficient excess of alkali to neutralise the oxidation product—



In this way the danger is avoided of adventitiously allowing the dyebath to become acid, with precipitation of the acid leuco compound. This principle applies irrespective of whether the conditions under which dyeing is carried out are most strictly controlled or are subject to no more than the good judgment of the dyer. The equation shows that rather less than one part of alkali is required to neutralise the oxidation product of two parts of hydrosulphite added—an elementary point which has, perhaps, been emphasised insufficiently in the past. It is therefore necessary to ensure that not less than this amount of alkali is always present in the dyebath, if necessary by making alkali additions at this ratio at the same time as hydrosulphite additions are made. If this procedure is carried out there is no difficulty in adjusting the addition of sodium hydroxide, the danger of acid leuco formation is avoided, and the complication of regulating the alkali and hydrosulphite additions independently is eliminated.

The control of hydrosulphite concentration is not so simple, although it must be agreed that the skilled dyer can achieve remarkably good results merely from the appearance of the dyebath and the use of Caledon Yellow paper. The basic data required for the control of this reagent are the rate at which it must be replaced and the properties of the dye which determine the minimum concentration of hydrosulphite necessary for successful dyeing. With this in view it is proposed to discuss—(a) the rate of oxidation of alkaline solutions of sodium hydrosulphite over a wide range of conditions and how these rates are related to typical practical systems, (b) the possibilities and practical limitations of potentiometric control of vat dyebaths, e.g. the Marhen process, and finally (c) some methods which may be generally applied to the measurement of the concentration of hydrosulphite in the bath.

Vat dyes are applied also to other fibres—wool, Ardil, cellulose acetate, etc.—from dyebaths which are less alkaline than is suitable for cotton dyeing, but these rather special applications will not be considered here.

Rate of Oxidation of Sodium Hydrosulphite

Before discussing methods of controlling hydrosulphite addition to the vat dyebath, we must examine the various factors affecting hydrosulphite oxidation during dyeing processes. A considerable number of experiments have been carried out with this object.

The primary reason for measuring oxidation rates was to obtain general information over a wide range of conditions, so that the results would be of some practical value rather than suitable for detailed analysis of reaction mechanism. This must therefore be considered as a preliminary study only.

EXPERIMENTAL

The experimental procedure was as follows. The required liquor but without the hydrosulphite, contained in a stainless-steel tank 15.2 cm. \times 17.1 cm. \times 25 cm. high, was agitated by circulation through a stainless-steel centrifugal pump of capacity 10 litres per minute. This liquor (1380 c.c.) was brought to the required temperature by means of an immersion heater, and the experiment started by the addition of the required amount of sodium hydrosulphite. Hydrosulphite from the same sample was used throughout the investigation in order to avoid possible differences due to trace-metal contamination, whose action is at present unknown. The bath was sampled at appropriate intervals with hypodermic syringes—a method which excludes air during sampling and prior to analysis and also enables the samples to be stored for a short period while awaiting examination. Analysis was by direct oxidation with alkaline potassium ferricyanide^{1,2} under air-free conditions in the microtitration apparatus described later. It had previously been ascertained that excess of sodium sulphite (the oxidation product of sodium hydrosulphite) does not interfere with the titration.

Preliminary experiments with and without stirring showed that when the bath was stirred the results were much more consistent and, as would be expected, the rate of oxidation was greater. In practice dyebaths are turbulent, and even the liquor in storage tanks is rarely left static. The subsequent experiments were therefore all carried out with pump agitation as described above. With the type of pump used the liquor flow remains constant providing that precautions are taken to ensure that the pump casing is free from air. Thus the degree of agitation was constant. It was also found that experiments carried out respectively with 15 g. Caledon Yellow GNS per litre, with 15 g. Caledon Brown RS per litre, and with no addition of dye gave results which did not differ significantly. All subsequent experiments were therefore carried out with 15 g. Caledon Yellow GNS per litre, with the exception of those with hydrosulphite concentrations of 2 g./litre and below, for which the dye concentration was 1.5 g./litre. The initial concentrations (wt./vol.) of sodium hydroxide and sodium hydrosulphite were equal.

The rate of oxidation of hydrosulphite solution padded on cloth was measured by noting the time required for complete oxidation, the end-point being determined colorimetrically with Caledon Yellow GN both as an external and as an internal indicator. There was no systematic difference between the two methods, and the mean was taken as the true value. In the experiments at 40°C. the material was padded directly into an air thermostat and therefore oxidised in a relatively still atmosphere. This was necessary to avoid drying the cloth. For the experiments at 20°C. air at this temperature was blown on to the fabric with an industrial-type "hair dryer", it being considered that a reproducible air flow would be more satisfactory than still air. The consistency and the reproducibility of the results showed that the air flow was sufficiently constant for the purpose.

The time required for complete oxidation plotted against the concentration of hydrosulphite used gave a smooth curve and reproducible results, and this was taken as giving a good representation of the true rate of decomposition.

EFFECT OF TEMPERATURE

The effect of temperature on the oxidation rate is considerable and is illustrated in Fig. 1.

It will be noted that, while an alkaline solution of sodium hydrosulphite is relatively stable when cold, it oxidises rapidly when hot. Under the present set of conditions, for example, at 80°C. 75% of a 40 g./litre solution is oxidised in 1½ hr., while at 20°C. only 6% is lost in the same time. It will be noticed, too, that the "decomposition" curves tend towards an exponential shape as the temperature increases, showing that the rate-controlling factors alter as the temperature is raised. The oxidation of sodium hydrosulphite is evidently a complex phenomenon, as is to be expected of this type of reaction.

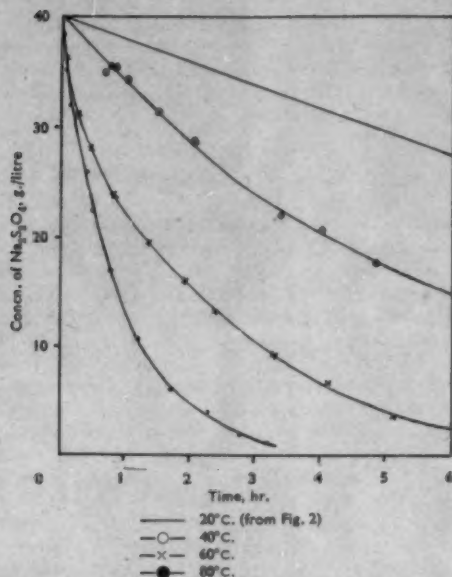


FIG. 1—Rate of Oxidation of Alkaline Sodium Hydrosulphite at Various Temperatures (specific surface exposed to air = 0.19 sq.cm. per c.c. of liquor)

It was also noted that in many of the experiments, particularly at low temperatures, there was a short but definite induction period before oxidation started. The significance of this observation is not known.

EFFECT OF CONCENTRATION

In the series of experiments at 20°C. with a range of concentrations of sodium hydrosulphite, it was noted that the plots of concentration against time gave parallel straight lines during the whole period of 6–7 hr. for which they were determined so long as the concentration remained greater than about 6 g./litre. The decomposition rate (the slope of the lines) in all these experiments was therefore independent of the starting concentration. Below this critical concentration the curve closely fitted an exponential function. By calculating the mean value of the individual slopes it was found that—

$$-\frac{dc}{dt} = 0.036 \text{ g./litre per minute for } c > 6 \text{ g./litre} \quad (i)$$

$$-\frac{dc}{dt} = (0.005c + 0.005) \text{ g./litre per minute} \quad \text{for } c < 6 \text{ g./litre} \quad (ii)$$

where c is the concentration of sodium hydrosulphite in grams per litre and t is the time in minutes. The resultant curve is given in Fig. 2 and the experimental points are fitted to it at the appropriate starting concentration; thus each series of points represents one experiment. It will be seen that the experimental points fit this composite curve satisfactorily.

The inferences implicit in this analysis are—

(a) The amount of hydrosulphite oxidised in a given period is the same in concentrated solutions as in more dilute solutions; the former are therefore proportionately more stable.

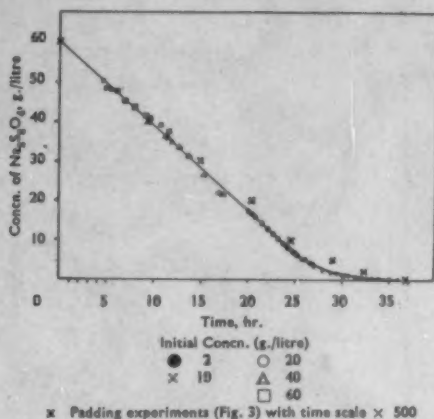


FIG. 2—Rate of Oxidation of Alkaline Sodium Hydrosulphite at 20°C. with Various Initial Concentrations compared with that of Hydrosulphite padded on Cloth

(b) The rate of oxidation does not appear to be retarded by the presence of the oxidation products, principally sodium sulphite, for a fresh solution decomposes at the same rate as an originally stronger solution containing an accumulation of the oxidation product. This indicates that the oxidation is irreversible, a view confirmed by the fact that the electrode potential of alkaline hydrosulphite solutions is unaffected by addition of sulphite (Gupta, unpublished results), which would not be the case if the reaction were reversible.

EFFECT OF ALKALI

Since the concentration of sodium hydroxide was the same as that of the sodium hydrosulphite, it varied considerably over the series of experiments. To check the extent to which it might affect the oxidation rate, a series of experiments was carried out with the ratio by weight of sodium hydroxide to sodium hydrosulphite ranging from 1 : 2 to 10 : 1. From the results it can be concluded that, provided that the bath contains excess of alkali, the oxidation rate is independent of caustic soda content.

RATE OF OXIDATION IN CHEMICAL PADDING

In pad-steam dyeing the pigment-padded cloth is impregnated with sodium hydrosulphite and caustic soda before passing into the steamer. To avoid excessive loss of hydrosulphite, it is generally recognised that the distance between the pad mangle and the steamer should be kept to a minimum. The extent of the oxidation, however, is not usually known, and the distance adopted is not based on precise knowledge.

Fig. 3 shows oxidation rates at 20°C. and 40°C. of hydrosulphite padded on cloth. It will be seen that the time axis is now measured in minutes or seconds rather than hours. The reason for the great increase in speed is obviously the very much greater specific surface. In fact, in the present case the geometrical surface of the liquor exposed on the cloth was 94 and 109 sq.cm. per c.c. of solution

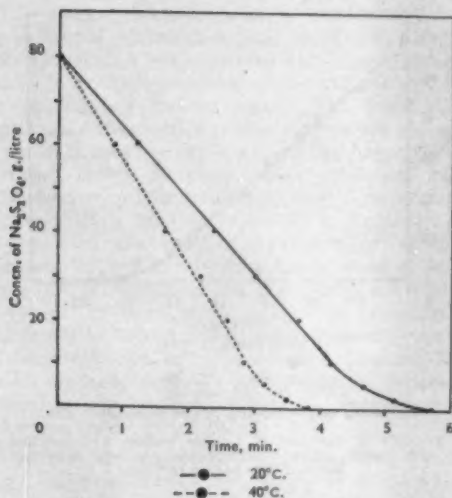


FIG. 2—Rate of Oxidation of Alkaline Sodium Hydrosulphite padded on Cloth

at 20°C. and 40°C. respectively (these figures were calculated by taking into account the liquor pick-up, cloth weight, etc., and ignoring such refinements as surface structure), whereas the experiments carried out in solution gave 0.19 sq. cm. of exposed surface per c.c. of solution. Thus the liquor padded on the cloth had a surface area 500 times as great as the equivalent volume of liquor in the experiments illustrated by Fig. 2, and might be expected to oxidise 500 times as rapidly. In Fig. 2 the large crosses are points from the 20°C. curve in Fig. 3 obtained after allowing for this factor of 500. In view of the sweeping simplifications made, the excellent agreement obtained here is undoubtedly partly fortuitous, but there can be no doubt that the surface area exposed is a factor of overwhelming importance in determining the extent of oxidation of hydrosulphite.

It will be seen from Fig. 3 that the hydrosulphite concentration of the liquor on the cloth fell at the rate of about 0.3 g./litre per second, and at higher temperatures the rate was considerably greater. If it is considered that a loss in concentration of up to 2 g./litre can reasonably be tolerated, then an air passage of 7 sec. would be permissible. This figure would be modified with lightweight fabrics, because of their larger specific surface, and at higher temperatures, because of the increased rate of oxidation, while with leuco padding the oxidation might be much faster. For general purposes, however, an air passage of up to 7 sec. has in practice been found satisfactory for all cold padding operations. It represents a distance of 3½ yd. at 30 yd./min., and a correspondingly greater distance at higher running speeds. Hot padding, as in leuco-padding techniques, necessitates a shorter air passage if excessive loss of hydrosulphite is to be avoided. The Standfast molten-metal machine, which eliminates the air passage entirely, solves this problem and is the only completely satisfactory method of leuco-padding vat dyes. It should be

noted that slow running speeds, pale dyeings with their lower hydrosulphite concentrations, light-weight cloths, and high chemical-padding temperatures all tend to increase the dangers of loss of hydrosulphite in padding operations.

JIG DYEING

In jig dyeing, sufficient hydrosulphite must always be present, not only to keep the dyebath in condition but also to prevent build-up of dye at the selvages due to oxidation at the exposed side of the batched roll. Obviously, different dyes and cloth constructions require different minimum concentrations of hydrosulphite, but the concentrations and temperatures used in jig dyeing are such that the rate of oxidation is no longer independent of concentration, as was the case in the previous example. By experience the dyer learns at what rate hydrosulphite must be added to achieve a satisfactory dyeing, but the actual concentration is rarely known. In one set of bulk-scale jig dyeings during which the hydrosulphite concentrations were measured (Wiltshire, private communication), it was established that so long as regular hydrosulphite additions were made the concentration rapidly came to an equilibrium value, which showed that the rate of oxidation for that concentration equalled the rate of addition. In two experiments at 50°C. and 70°C. the equilibrium concentrations were found to be 4 and 2.5 g./litre respectively, the difference in concentration arising from the effect of temperature on the oxidation rate. It has frequently been noted qualitatively that more hydrosulphite is required in small-scale laboratory jigs than under corresponding conditions in bulk working. The reason is evidently that, although the liquor ratio is the same, and the linear dimensions are strictly proportional, the surface area of the liquor and the exposed surface of the cloth are relatively greater in the smaller jig. Measurements on the laboratory jig and the bulk-scale jig at 50°C. and on the latter at 70°C. are collated in Table I with the oxidation rates at 20°C. as given by equation (ii). The relative surface areas in these experiments were 1.4, 0.43, and 0.19 sq.cm./c.c. for the small-scale laboratory jig, the bulk-scale jig, and the experiments described by equation (ii) respectively. On the assumption of direct proportionality, the corresponding rates have been calculated for unit specific surface, and are given in the last column of Table I.

TABLE I
Rate of Oxidation of Sodium Hydrosulphite in Jig Dyeing

Method	Temp. (°C.)	Mean Equi- librium Concn. (g./litre)	Rate of Oxidation (= rate of addition)	
			Measured (g./litre per min.)	Corrected (g./litre-min. sq.cm./c.c.)
Laboratory jig	50	2	0.25	0.18
Bulk-scale jig	50	4	0.15	0.35
	70	2.5	0.15	0.35
Laboratory experiments	20	2	0.015	0.08
	20	2.5	0.0175	0.092
(equation (ii))	20	4	0.025	0.13

It will be seen that in both jigs the oxidation rate at 50°C. is greater than that measured independently at 20°C. by a factor of ~2.5, while for 70°C. the factor is 3.8. These values are in reasonably good agreement with the temperature coefficient which might be expected for a chemical reaction of this nature.

CONCLUSIONS

In this study large approximations have been made for the sake of simplification, but in spite of this the principal conclusions emerge that, under practical conditions of use, rate of oxidation of hydrosulphite is proportional to the surface exposed to the air, and increases rapidly with temperature.

Electrometric Control of the Dyebath

For an understanding of the possibilities and the limitations of this method of dyebath control an outline of the oxidation-reduction properties of vat dyes may be given. These properties have recently been the subject of considerable examination⁸⁻¹⁰. By electrochemical methods it is possible to measure to what extent a vat dye can be reduced in any particular system. The "leuco potential"^{8,9}, which has been found to be the most satisfactory criterion in the normal alkaline aqueous bath, is defined as the potential at which the leuco vat dye is in equilibrium with a saturated solution of the oxidised form, i.e. is at the point of incipient oxidation. Ideally, the potential E in such a solution should obey equation (iii)—

$$E = E_0 - \frac{RT}{anF} \ln [\text{Red}] \quad (\text{iii})$$

where E is the leuco potential; E_0 is a constant for the dye related to its solubility and redox potential; n is the number of electrons added in the reduction (generally two); α is a measure of the reversibility of the reaction; $[\text{Red}]$ is the molar concentration of leuco dye; and R , T , and F have their usual significance. Thus the "leuco potential",

unlike the redox potential, depends on concentration; but the former, in spite of this disadvantage, is of much greater value in practice. Marshall and Peters⁸ have measured these potentials at widely differing concentrations for a number of dyes. The results calculated for three dyes by means of equation (iii) are illustrated in Fig. 4.

The three vat dyes were chosen to represent the extremes of the anthraquinone types, and include the most difficultly and the most easily reduced of those measured. Caledon Brown R and Caledon Red BN behave in a relatively straightforward manner with a value for α in the neighbourhood of unity, and their potentials differ by a constant amount over the complete concentration range. Caledon Brilliant Violet R, on the other hand, has a potential very much more dependent on concentration because of the smaller value of α . As a result, this dye has a more negative potential than Caledon Brown R, and is therefore more difficult to reduce, at all concentrations above 0.006 M. (at which the curves cross), but below this concentration the potential is more positive and the Violet is more easily reduced. Similarly, Caledon Red BN is more easily reduced than either of the other two dyes at all concentrations. These curves clearly show the most positive potentials at which the dyes will remain in solution at any particular concentration. A similar curve of potential against concentration for sodium hydrosulphite is also shown in Fig. 4. Since this compound does not give thermodynamically reversible potentials, the results in Fig. 4 were obtained only after a careful examination of the system^{6,8}; but it is considered that these potentials do give a good indication of the reducing power of hydrosulphite solutions, although the true values may even be 20–30 mv. more negative.

To keep a dyebath in condition it should, therefore, only be necessary to have sufficient hydrosulphite present to ensure that the required minimum potential is maintained. From Fig. 4 it can be seen that this should present no difficulty. At first sight the simplest and most elegant method of doing this would be by measuring the potential. This is the theoretical principle underlying the Marhen process¹¹. Unfortunately, in practice there are a number of difficulties. In the first place, measurement of the true potential requires a great deal of care, and if sufficient time is not allowed for a steady value to be reached, entirely erroneous results will be obtained. For example, each potential measured for the curve shown in Fig. 4 took over 6 hr. to become steady. Fig. 5 illustrates the rate at which a constant value was reached in one set of experiments.

It will be seen that the rate at which a steady value is reached not only is slow but also depends on the composition of the dyebath. Thus after 15 min. the potential registered is -1.08, -1.13, or -1.14 v. according to the amount of anthraflavic acid present. The final steady value reached was -1.153 v. It is easy to show that the slow change in potential is due to the slow response of

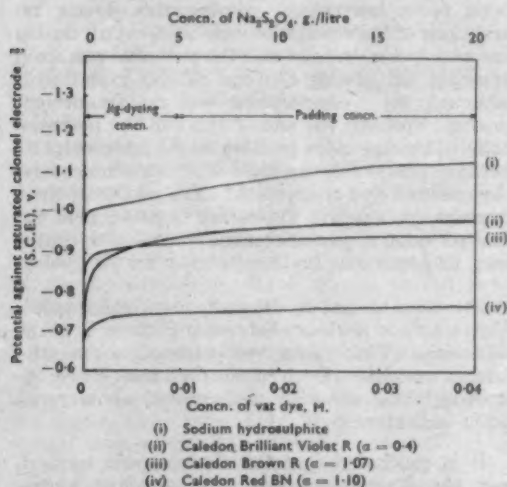


FIG. 4.—Effect of Concentration on the Leuco Potential of Vat Dyes and the Reduction Potential of Sodium Hydrosulphite at 60°C.

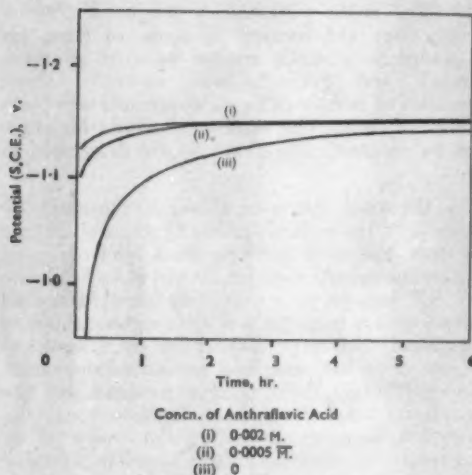


Fig. 5—Effect of Anthraflavic Acid on Speed of Response of the Platinum Electrode (20 g. sodium hydrosulphite + 20 g. sodium hydroxide per litre at 60°C. under oxygen-free nitrogen)

the electrode and not to a change in the reducing power of the dyebath, for, after the electrode has been removed, washed, and returned to the solution, the same slow curve is retraced. Furthermore, the same final value of the potential always seems to be approached irrespective of the additive, the effect of which is only to increase the speed of response of the electrode and not to alter the final potential.

On the other hand, if one tries to measure the potential of a dyebath when the hydrosulphite is undergoing oxidation—as usually occurs in practice—the potential becoming more negative is no guarantee that the hydrosulphite is being fed too quickly, but may merely indicate that the electrode has not yet reached equilibrium; in fact, the concentration may actually be falling as the electrode slowly approaches its most negative potential. Numerous experiments carried out in these laboratories have all led to the conclusion that it is not possible, by potentiometric means, to measure the true reducing power or the concentration of hydrosulphite during dyeing by any practical method except when the concentration is so low that the hydrosulphite is completely oxidised and the potential changes abruptly to a much more positive value. In such circumstances the warning may well be too late. In any case, inspection of Fig. 4 will show that hydrosulphite is so powerful a reducing agent that the amount required to maintain even the most difficultly reducible dyes in solution is extremely small.

It follows from the above and the experiments on rate of oxidation that the controlling factors that determine the lowest concentrations of hydrosulphite that can be successfully used in any particular dyeing methods are the rate of oxidation of the hydrosulphite, the rates of oxidation and re-reduction of the dye, and the concentration necessary to avoid localised depletion of the hydrosulphite, e.g. at the exposed liquor surfaces

and the selvages of the batching rolls in jig dyeing. Therefore control of hydrosulphite in dyeing should be applied not with the object of maintaining a constant potential but of maintaining a constant hydrosulphite concentration. Thus the addition of hydrosulphite is determined by the rate of oxidation at the lowest concentration which can be satisfactorily used.

At the same time as this conclusion was reached the Marhen process¹¹ was announced in the U.S.A. The principle of this process is that the dyebath potential is measured between a bright platinum electrode and a calomel reference half-cell, and hydrosulphite is fed at the rate necessary to maintain that potential at a predetermined value. In view of this development, a number of dyeings were carried out on the laboratory-scale automatic jig¹². During these dyeings measurements of potential and hydrosulphite analyses were made under a variety of conditions. In all the experiments a significant difference in potential was noted only when a 100% excess of hydrosulphite over normal requirements was used, apart from one occasion, when the sodium hydroxide was inadvertently omitted. Two of the experiments are illustrated in Fig. 6 and 7. In these experiments the potential was measured at a bright platinum electrode against a saturated calomel electrode by means of a pH-meter (Electronic Instruments Ltd. Model 23) and continuously recorded on a Kent recorder. The hydrosulphite concentration was determined on the polarograph¹³. The dyeings were 20% Caledon Blue XRCs.

In Fig. 6 the normal additions of hydrosulphite were made. It will be noted that, after the potential had reached a reasonably steady value, it remained constant throughout the run, and there was not even a fluctuation when the hydrosulphite additions were made in the usual way to keep the dyebath in correct condition. Fig. 7 is, perhaps, even more interesting. During this dyeing no additions of hydrosulphite were made at all during the run, but in spite of this the potential remained constant till almost the end of the experiment, although the hydrosulphite was rapidly decomposing. Towards the end of this run the potential rapidly became more positive as the hydrosulphite became completely oxidised and, simultaneously, the oxidised dye precipitated. The results of these experiments confirm the earlier impression of the limited value of potentiometric control of dyebaths and, in particular, its unsuitability for jig dyeing.

Attention should be drawn to one further point: Fig. 4 makes it clear that, even if there were no difficulties in measuring the potential, a potentiometric method is intrinsically insensitive to hydrosulphite concentration except as an end-point indicator.

It is concluded that the electrometric method, e.g. the Marhen process, of controlling hydrosulphite in dyeing processes is limited in its application to processes carried out at high

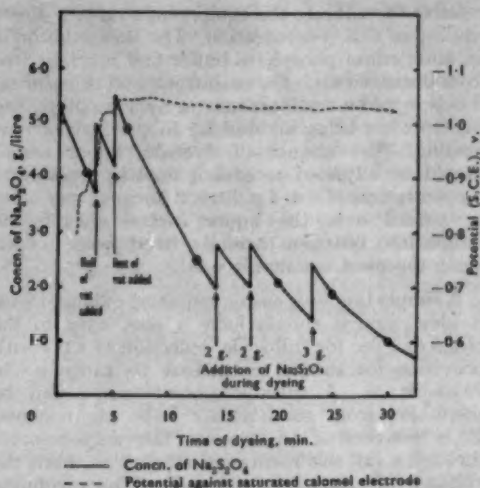


FIG. 6—Potential developed at a Platinum Electrode and Sodium Hydrosulphite Concentration measured during a Laboratory Jig Dyeing at 50°C. with Caledon Blue XRC—Additions of hydrosulphite made during the Dyeing according to the Normal Procedure

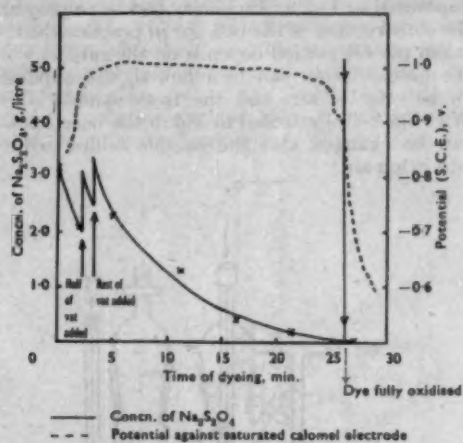


FIG. 7—Potential developed at a Platinum Electrode and Sodium Hydrosulphite Concentration measured during a Laboratory Jig Dyeing at 50°C. with Caledon Blue XRC—No Addition of Hydrosulphite during Dyeing

temperatures (which assist in accelerating the slow electrode reaction) and at very low hydrosulphite concentrations. The Williams unit¹⁴ is the outstanding process with which the Marhen method is used successfully. The electrode is placed a few inches below the liquor surface, and the feed rate of the hydrosulphite, which should be fed continuously, is gradually reduced until the potential takes up a value of -1.0 to -0.9 v., indicating incipient oxidation at the top of the Williams unit. Since oxidation is always greatest at the surface, the liquor in the bulk of the unit is maintained in good condition with respect to hydrosulphite. The actual concentration, of course, depends on a number of factors, probably least of all on the potential, which is itself no indication of the reducing power of the dyebath, but is merely a

qualitative indication that there is still a small excess of hydrosulphite present in the vicinity of the electrodes, information which the trained dyer obtains from the appearance of the surface of the dye liquor.

An application of potentiometric control to continuous dyeing by the pad-steam process¹⁵ has been proposed more recently. It is, of course, quite useless to measure the potential of the cold chemical-pad liquor, but in this latest proposal the difference in potential between two electrodes on the cloth, inside the entrance of the steamer and at the exit respectively, is measured. It is claimed that when a large difference in potential is observed the resultant dyeing is weak—the hydrosulphite having been so deficient that it has been completely decomposed in the steamer. This method appears to have distinct possibilities, particularly if the second electrode is judiciously placed so that there is sufficient hydrosulphite for full fixation but not so much that there is an excessive consumption of oxidising agent in the after-treatment boxes. The same information is, of course, obtained from the speed at which the leuco dye is oxidised, which can usually be seen from the change in colour during passage through the washing range.

The two examples quoted show that the potentiometric method is limited to qualitative control under restricted conditions only, and cannot be considered a panacea for controlling hydrosulphite additions to vat dyebaths.

The Measurement of Hydrosulphite Concentration in Vat Dyebaths

Quantitative estimation of sodium hydrosulphite content is the only method of control which can be applied unambiguously to all systems of dyeing, and analytical methods must be the final criterion when the more indirect tests of potential, Caledon Yellow GN paper, and dyebath appearance fail or give inconsistent results. The most convenient methods are based on the use of—

(a) The polarograph, which gives a meter reading of the concentration, and is outstanding in rapidity of measurement; unfortunately, although simple to use and maintain, it is perhaps not entirely suitable for normal dyehouse use

(b) The Vat-o-meter, a remarkably simple device which depends on the volume of air oxidised by a given amount of dye liquor

(c) Direct titration of a sample from the dyebath with a convenient oxidising agent.

Each of these methods will be briefly discussed.

THE POLAROGRAPH

The polarography of sodium hydrosulphite has been fully described by Furness¹⁶, but to many it is probably an unfamiliar technique, and in view of its increasing interest and the novelty of the method in the field of dyeing technology the principle will be outlined.

Hydrosulphite is electrolytically oxidised at a dropping mercury electrode, and under the correct conditions of electrolysis the concentration at the

surface of the mercury is zero. As a result, the electrolytic current is proportional to the rate at which the hydrosulphite can diffuse to the electrode, and this in turn is proportional to the concentration in the bulk of the solution. Thus the polarographic (or electrolytic) current i is proportional to the concentration c of oxidisable material—

$$c = ki \quad \text{(iv)}$$

where k is a constant, an approximate value of which can be calculated from the Ilkovič equation¹⁰. This equation has been found to hold for a large proportion of the substances which can be oxidised or reduced at a dropping mercury electrode. Naturally, the conditions of potential, base solution, and concentration must be properly chosen if interference from other oxidisable or reducible substances is to be avoided.

A commercial polarograph is an expensive piece of apparatus, but if hydrosulphite estimations only are required, simple equipment will give equally satisfactory results. The many refinements in modern commercial instruments are unnecessary for this purpose and may only lead to confusion.

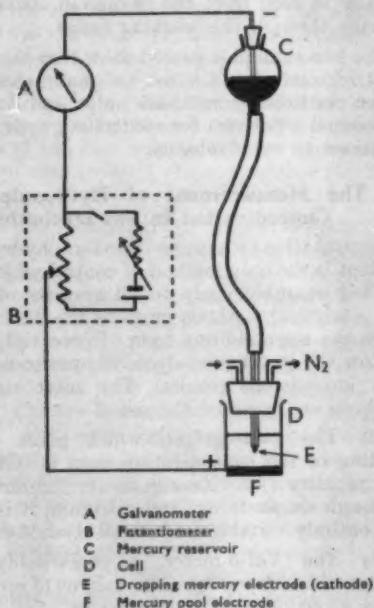


FIG. 8—Diagrammatic Representation of the Polarograph

The basic equipment (Fig. 8) consists of four essential parts—(a) the polarograph cell, including the mercury pool electrode, (b) the dropping mercury electrode, which is connected to a mercury reservoir, (c) the potentiometer, which applies a potential between the two electrodes through (d) the galvanometer. In carrying out a measurement the potential is adjusted to -0.3 v., and the current is noted before and after the unknown hydrosulphite solution is added to the base solution in the cell. The increase in current is proportional to the hydrosulphite concentration, and it is

possible to calibrate the equipment to give a direct reading of this concentration. The base solution is an ammonium phosphate buffer and must be free from dissolved air. The easiest method of ensuring this is to add a small amount of hydrosulphite, the slight excess being allowed for in the first current reading. The aliquot of dyebath liquor added should be adjusted to give a final hydrosulphite concentration of $0.1-1$ g./litre. An inert gas must be passed over the liquor surface during the estimation, nitrogen carefully freed from oxygen being the most commonly used.

A simple taut-suspension reflecting galvanometer is ideal, and it should have a sensitivity in the range of $1 \mu\text{a.}$ for full-scale deflection (F.S.D.) with provision for shunts to increase its range up to $50 \mu\text{a.}$ F.S.D. A suitable potentiometer can be assembled from good-quality radio components. It is convenient to connect the galvanometer through a suitable resistance network to check the voltage of the potentiometer. The dropping electrode and the cell can be readily constructed in the laboratory. The cell may consist of a bottle fitted with a rubber bung with suitable fittings or a more elaborate cell such as is illustrated in Fig. 9. Ingenuity can be employed in the construction of the cell, for in practice the time taken per estimation depends on the rate at which the base solution can be renewed, the apparatus swept clear of air, and the fresh sample added. With the cell illustrated in Fig. 9 the base solution can be changed and the sample added without admitting air.

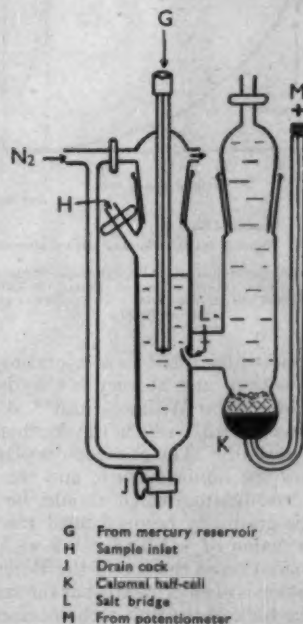


FIG. 9—Polarograph Cell suitable for Rapid Routine Measurements

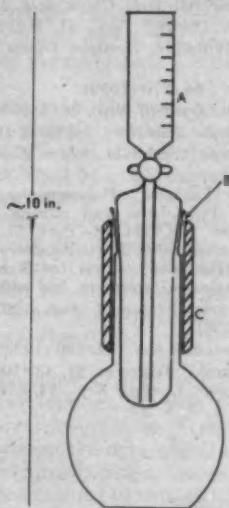
Before using this method of estimation, it is very advisable to have a good understanding of the system, and one of the excellent treatises on the

subject should be consulted¹⁷, but the foregoing description gives some idea of the simplicity of the method.

The polarographic method is ideal for the estimation of hydrosulphite under suitable conditions and is probably the fastest and most convenient method available. So far as the average dyehouse is concerned, however, it suffers from two disadvantages—it requires a supply of oxygen-free nitrogen and very pure mercury. Both are easy to provide so long as they are required regularly, but it is difficult to cater for intermittent use. Furthermore, satisfactory operation depends on thorough understanding by the supervising personnel, and it is frequently difficult for busy technicians to acquire the necessary background.

THE VAT-O-METER

The Vat-o-meter¹⁸ need be mentioned only briefly. The equipment, which is very simple, is shown in Fig. 10. An aliquot of dye liquor is added to the apparatus together with a foaming agent, the tap is closed, and the whole apparatus is shaken vigorously for a fixed time. Water is added to the graduated measuring cylinder, the tap opened, and water run in to equalise the pressure. The volume added represents the volume of oxygen absorbed, and the apparatus can be calibrated directly in terms of hydrosulphite concentration. The neck of the flask where it is held in the hands is provided with a cork insulating band to minimise temperature effects.



- A Graduations calibrated in grams of sodium hydrosulphite per litre
- B Quickfit joint
- C Cork insulation

FIG. 10—The Vat-o-meter

An alkaline solution containing 14.5 g. sodium hydrosulphite per litre will absorb its own volume of oxygen. It can be seen, therefore, that it is likely that this method will have its limitations at lower concentrations, of the order of 1–3 g./litre. One would expect it to be well suited to the

concentration of hydrosulphite used in the pad-steam process. Royer² reports a figure of $\pm 20\%$ for its reproducibility at a concentration of 8 g./litre, which is sufficiently accurate for many of its applications.

TITRATION OF HYDROSULPHITE SOLUTIONS

Titration of an aliquot of the dyebath solution with a suitable oxidising agent is a convenient and direct method of estimation. Precautions must be taken, however, to exclude air. Freshly boiled-out or otherwise de-oxygenated water should be used in the titration vessel. Alkaline potassium ferrieyanide and sulphonated Indigo^{1,2} have been found suitable as oxidising agents, and experience has shown the former to be entirely satisfactory.

For occasional titration, the easiest method has been found to be to carry out the titration in a 250-ml. beaker to which freshly boiled-out water is added and covered with a layer of liquid paraffin. An aliquot of the dyebath is entered by placing the tip of the pipette or syringe below the paraffin layer and the titration is carried out in the usual way, but with the tip of the burette below the liquor surface. The liquid is stirred with a battery-driven magnetic stirrer.

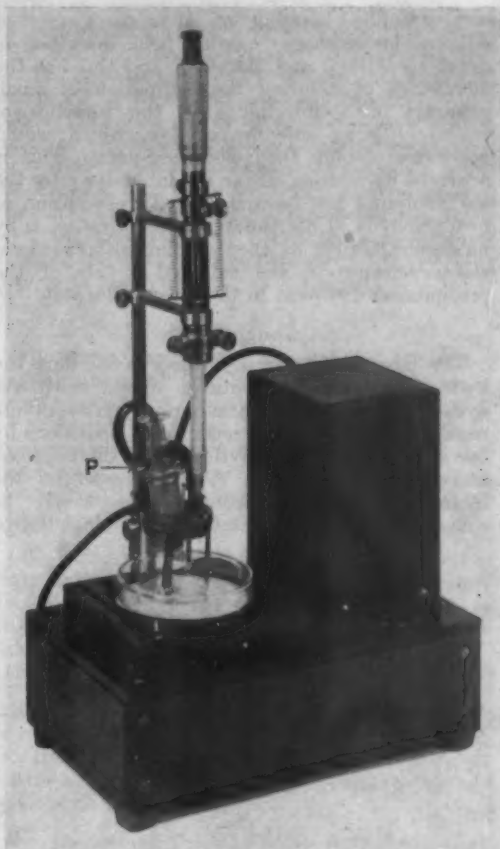


FIG. 11—Microtitration Apparatus

The more refined microtitration apparatus (Fig. 11) was developed in these laboratories to be self-contained, portable, and rapid in use, so that problems concerning the use of hydrosulphite could be examined on the spot. It uses a flow-through type of cell, which allows the liquor to be changed without exposing it to the air. The titration cell is kept full, thus obviating the need for liquid paraffin, the volume displaced by the titrant being taken up by the plunger *P*. The titration is carried out by means of a micrometer syringe, and magnetic stirring is used. Caledon Yellow GN is used as an internal indicator whenever possible, but when the dye concentration in the dyebath is so great that the colour change is obscured, an electrometric end-point can be obtained, using a portable pH-meter as indicator, but replacing the glass electrode with a platinum electrode. Owing to the slowness of the electrode response, the visual end-point is much preferred for accuracy and speed.

This short résumé is not exhaustive, and there are other methods of hydrosulphite estimation, e.g. Merriman's method¹⁹, involving neutralisation and addition of formaldehyde to form the sulphonylate, which is then estimated iodometrically.

A simplified version of Merriman's method adapted for dyehouse use has been described in detail by Airoidi and Marchi²⁰, and this has the advantage of allowing the estimation of small amounts of hydrosulphite in the presence of relatively large amounts of dye, which would otherwise obscure the visual end-point. This is achieved by filtering off the insoluble dye after the hydrosulphite has been stabilised by addition of formaldehyde. Unfortunately, this filtration is by no means always as easy as the authors would assume, owing to the colloidal nature of the precipitated dye even in the presence of salt.

Conclusion

The best method of accurately controlling the hydrosulphite requirements in dyeing with vat dyes is to determine the minimum hydrosulphite requirements for the particular local conditions by one or other of the analytical methods described and subsequently make routine checks on the hydrosulphite concentration. This would be sufficient to ensure the maintenance of a high degree

of efficiency. Naturally, continuous recording of the concentration would be most useful, but at the moment there is no simple method available for carrying this out. It is also possible in certain circumstances to use potentiometric control (the Marhen process) by judiciously placing the electrodes near the surface of the liquor, and this has the great advantage of being readily amenable to automatic control. In using potentiometric control it should be clearly understood that it is qualitative, and there is no unique relation between the recorded potential and the concentration of sodium hydrosulphite.

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COMMUNICATIONS

The Identification of Vat Dyes

D. A. DERRETT-SMITH and J. GRAY

The tables published in 1940 by Derrett-Smith and Bradley¹ and in 1947 by Derrett-Smith and Gee² have been brought up to date to include all the British, German, and Swiss vat and solubilised vat dyes which have appeared on the British market since 1940. Dyes which were included in the original tables but have since been made by other firms are included under their new names.

In addition, it is shown that certain vat dyes behave differently when treated with sodium hydrosulphite and sodium hydroxide as compared with sodium hydrosulphite and sodium carbonate.

Introduction

Four colour reactions of some 900 British, Swiss, and German vat dyes were tabulated and classified in 1940, as an aid to identifying vat dyes on linen and cotton materials¹. The first two of the colour reactions take advantage of the fact that the colours of the dye in its reduced condition with alkaline and acid hydrosulphite are characteristic of certain chemical groups of vat dyes. These colours, and the colours in sulphuric and nitric acids, are in most cases sufficient to enable an individual dye to be identified.

In some of those cases where the vat dyes are not easily identified by these reagents, an additional test has been found useful, viz. the reaction with acid potassium permanganate solution².

Since the original tables were published, a large number of new vat dyes have appeared on the market, while many of the vat dyes already listed have been marketed by other manufacturers under their own trade names. In view of these developments, the tables have now been brought up to date, and include both the new and the newly named British, Swiss, and German vat dyes. Solubilised vat dyes under the following trade names have been added—Cibantine dyes (Ciba), Sandozol dyes (S), and Tinosol dyes (Gy).

The present paper giving these new tables is divided into two sections. Section I contains dyes which are equivalents of those given in the original tables, and includes 175 dyes which are the equivalents of 70 dyes already listed; the original numbering has been maintained in this section.

Section II contains a list of the new vat dyes, and equivalent dyes are grouped together; the list includes 139 dyes, giving 89 groups of equivalent dyes. The numbers given to these new dyes are the same as those of the last members of their respective groups in the original tables; to distinguish them, the numbers of the new dyes are given a suffix—*a*, *b*, or *c*. For example, No. 170*a* and 170*b* are blue vat dyes giving a blue colour with the alkaline hydrosulphite reagent; the last of this group in the original tables was numbered 170.

As before², colour reactions with acid potassium permanganate are quoted only where they provide useful further information.

Section I

Dyes equivalent to those already listed

NOTE

The solubilised vat dyes Indigosol Bordeaux I2RN, Cibantine Bordeaux 2RN, Tinosol Bordeaux 2RN, and Sandozol Bordeaux 2RN are equivalent to Ciba Bordeaux 2RN (No. 86). In each case the colour given with acid hydrosulphite is green-yellow, but with heavy dyeings the dye is not completely reduced to this colour even on boiling for several minutes, the brown-red colour given in the original tables being produced. The true green-yellow colour of the acid leuco compound can, however, be obtained from heavy dyeings by first reducing under alkaline conditions and then acidifying with acetic acid.

CORRIGENDA

(1) Durindone Brown G (No. 255) is listed in the original tables as giving with acid hydrosulphite a brown colour which is stripped. The true colour of the acid leuco compound is, however, yellow. It is given quickly with pale dyeings but more slowly with heavier dyeings; boiling for several minutes is necessary with deep colours. There is no stripping action.

(2) Indigosol Brilliant Green IBA is listed in the original tables with Algal Brilliant Green BK under No. 235. These dyes are not equivalent. Indigosol Brilliant Green IBA should be listed with Caledon Jade Green XS under No. 213. Indigosol Green AB is the equivalent of Algal Brilliant Green BK.

(3) Indanthren Printing Violet BF is listed in the original tables with Caledon Purple RS under No. 104. These dyes are not equivalent, and Indanthren Printing Violet BF should be listed separately under 124*a*.

(4) Indanthren Printing Black B (No. 333) and Indanthren Printing Black BL (No. 335) were inadvertently reversed in the index to the original tables.

TABLE I
Yellow and Orange Dyes

No.	Dye	Hydrosulphite Alkaline	Acid	HNO ₃	H ₂ SO ₄	Acid KMnO ₄
		BLUE-RED OR RED-VIOLET				
1	Paradone Golden Yellow RK Cibanone Golden Yellow RK Cibantine Golden Yellow RK Tinon Chlorine Golden Yellow RK Tinosol Golden Yellow RK Sandothrene Golden Yellow NRK Sandozol Golden Yellow RK	Blue-red	Red-yellow	Red-yellow Violet
4	Indigosol Orange I8R Cibantine Orange 8R Sandozol Orange 8R	Red-violet	Brown-red	Brown-red Blue
6	Paradone Orange RRT Indigosol Golden Orange I2R Cibantine Golden Orange 2R Tinon Chlorine Golden Orange 2R Tinosol Golden Orange 2RL Sandozol Golden Orange 2R	Red-violet	Brown-red	Brown-red Blue
		VIOLET				
8	Indigosol Yellow GC	Violet	Red-yellow	Green-yellow Green-yellow
9	Cibanone Brilliant Orange GK Tinon Chlorine Brilliant Orange GK Sandothrene Brilliant Orange NGK	Violet	Red-yellow	Red-yellow Yellow-green
10	Paradone Brilliant Orange RK Cibanone Brilliant Orange RK Cibantine Brilliant Orange RK Tinon Chlorine Brilliant Orange RK Tinosol Brilliant Orange RK Sandothrene Brilliant Orange NRK Sandozol Brilliant Orange RK	Violet	Red-yellow	Red-yellow Yellow-green
		GREEN				
18	Paradone Brilliant Orange GR	Yellow-green	Black-green	Red-yellow Red-yellow
		YELLOW				
21	Cibantine Orange R Tinosol Orange R Sandozol Orange R	Green-yellow	Yellow-red	Yellow-red Violet
22	Tinosol Yellow CG...	Green-yellow (almost de- colorised)	Green-yellow	Brown-yellow Red-violet
		RED				
28	Caledon Yellow 3R Soledon Yellow 3R Cibanone Yellow 3RF Tinon Chlorine Yellow 3RN	Yellow-red	Grey-green-yellow	Red-yellow Black-violet
29	Paradone Yellow 3RT	Yellow-red	Grey-green-yellow	Red-yellow Black-violet
31	Caledon Golden Yellow GK Paradone Golden Yellow GK Cibanone Golden Yellow GK Cibantine Golden Yellow GK Tinon Chlorine Golden Yellow GK Tinosol Golden Yellow GK Sandothrene Golden Yellow NGK Sandozol Golden Yellow GK	Red	Yellow	Red-yellow Red-violet

TABLE I (contd.)

Yellow and Orange Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
		Alkaline	Acid			
RED (contd.)						
39	Cibanone Yellow 5GK Cibantine Yellow V Tinson Chlorine Yellow 5GK Tinosol Yellow V Sandothrene Yellow N5GK Sandozol Yellow V	Black-red	Green-yellow	Green-yellow	Yellow	—
BROWN						
41	Caledon Printing Yellow 6G	Yellow-brown	Green-grey	Yellow	Yellow-red	—
42	Cibanone Golden Orange 3G Tinson Chlorine Golden Orange 3G Sandothrene Golden Orange N3G	Brown	Brown-yellow	Red-yellow	Green-blue	—
BLACK						
46	Tinson Chlorine Yellow GKN Sandothrene Yellow NGKF	Red-grey	Yellow	Yellow	Grey-yellow	—

TABLE II

Red Dyes

No.	Dye			Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
				Alkaline	Acid			
VIOLET								
60	Paradone Scarlet GK	Violet	Brown-yellow	Red	Yellow-green	—
BLUE								
63	Tinon Chlorine Rubine R	Green-blue	Black-blue-red	Yellow	Yellow-red	—
GREEN								
64	Paradone Scarlet 2G	Yellow-green	Black-green	Yellow-red	Yellow-red	—
YELLOW								
67	Cibantine Scarlet 3B Tinosol Scarlet 3BL Sandozol Scarlet 2B	Green-yellow	Red	Red	Green	—
73	Cibantine Red 3BN Tinosol Red Violet RH Sandozol Red Violet RH	Green-yellow	Grey-blue-red (stripped)	Blue-red	Green	—
74	Cibantine Brilliant Pink 2BG	Green-yellow	Yellow (stripped)	Blue-red	Green	—
76	Paradone Brilliant Pink R Cibantine Brilliant Pink R Tinon Brilliant Pink R Tinosol Pink R Sandozol Pink R	Green-yellow	Red	Red	Red (on fibre); bleeds green after a time	—
77	Tinon Brilliant Pink B	Green-yellow	Red	Red	Red (on fibre); bleeds green after a time	—
78	Cibantine Scarlet 2B Tinosol Scarlet B Sandozol Scarlet B	Green-yellow	Red (stripped)	Yellow-red	Violet (on fibre); bleeds black-blue after a time	—

TABLE II (contd.)

Red Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
		Alkaline	Acid			
YELLOW (contd.)						
79	Tetra Scarlet 2B	Green-yellow	Red (stripped)	Yellow-red	Red-violet (on fibre); bleeds black-green after a time	—
81	Durindone Printing Magenta B...	Green-yellow	Blue-red (stripped)	Blue-red	Red-violet	—
82	Cibantine Brilliant Pink 3B Tinosol Brilliant Pink 3B	Green-yellow	Blue-red	Red	Red	—
83	Sandothrene Brilliant Pink 2B ...	Green-yellow	Blue-red	Red	Blue-red (on fibre); bleeds green after a time	—
86	Indigosol Bordeaux I2RN Cibantine Bordeaux 2RN Tinon Bordeaux 2RN Tinosol Bordeaux 2RN Sandozol Bordeaux 2RN	Green-yellow	Green-yellow (may be brown-red in heavy dyeing)	Black-red	Blue-grey	—
89	Paradone Brilliant Scarlet RK ...	Red-yellow	Yellow-red	Green-yellow	Yellow-red (on fibre); bleeds red-yellow	—
BROWN						
92	Tinon Bordeaux 2B	Red-brown	Brown	Black-red	Grey, then brown-green	—
BLACK						
103	Caledon Brilliant Red 3B Cibanone Red FBB Cibantine Red FBB Tinon Chlorine Red F2B Tinosol Red F2B Sandothrene Red NF2B Sandozol Red F2B	Brown-black	Red-yellow	Red	Grey-yellow (almost decolorised)	—

TABLE III

Violet Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄	
		Alkaline	Acid				
BLUE							
106	Paradone Brilliant Violet 3B	Blue	Blue-red	Violet	Yellow-green	Violet-grey
106a	Caledon Brilliant Violet 3B	Blue	Blue-red	Violet	Yellow-green	Yellow-grey
108	Sandothrene Violet N2RB	Green-blue	Red-violet	Red-violet	Green	---
109	Paradone Brilliant Violet 4R ... Cibantine Brilliant Violet 4R Sandozol Brilliant Violet 4R	...	Green-blue	Red-violet	Red-violet	Green	---
YELLOW							
123	Cibantine Violet 6R ... Sandozol Printing Purple R	...	Red-yellow	Brown, then grey-green	Red-violet	Green	---

TABLE IV

Blue Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
		Alkaline	Acid			
		VIOLET				
130	Tinon Chlorine Dark Blue BOA	... Violet	Brown-red	Red-black	Red-violet	Yellow-brown
133	Tinon Chlorine Dark Blue MBA	... Violet	Brown-red	Red-black	Violet	Brown
134	Sandothrene Dark Blue NMB	... Violet	Brown-red	Red-black	Violet	Brown
		BLUE				
137	Paradone Navy Blue G	... Blue	Blue-red	Black-green	Blue-red	Brown
142	Paradone Navy Blue R	... Green-blue	Blue-red	Blue-green, then black	Red-violet	Brown-green
143	Alizanthrene Navy Blue RT	... Green-blue	Red-violet	Black-blue	Red-violet	—
146	Paradone Brilliant Blue 3G	... Blue	Violet	Yellow	Green-brown	Green-yellow
149	Paradone Brilliant Blue R Cibanone Brilliant Blue R	... Blue	Violet	Yellow	Green-brown	Yellow-green
159	Tinosol Blue BC Sandozol Blue BC	... Blue	Blue	Green, then yellow	Green-brown	Green-blue
163	Cibantine Blue GF	... Blue	Blue	Green, then yellow	Green-brown	Green-blue
168	Paradone Blue Green FFB	... Blue	Blue-red	Black-green	Black-brown-green	Yellow-green
		YELLOW				
179	Indigo 2R	... Green-yellow	Grey-blue (stripped)	Red-yellow	Blue-green	—
185	Cibantine Blue 2G	... Green-yellow	Blue (stripped)	Blue-green, then brown-yellow	Blue-green	—
188	Cibantine Blue 2B Tinosol Blue O4B Sandozol Blue O4B	... Red-yellow	Green-blue (stripped)	Black-blue, then brown, then red-yellow	Blue-green	—

TABLE V

Green Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
		Alkaline	Acid			
		BLUE				
214	Cibantine Brilliant Green BF Tinon Chlorine Brilliant Green BF Tinosol Green B Sandothrene Brilliant Green NBF Sandozol Green B	... Blue	Blue-red	Grey-green, then yellow-brown	Blue-red	Brown
215	Indanthren Brilliant Green 3B Sandothrene Brilliant Green N2B Tinon Chlorine Brilliant Green 2B	... Blue	Blue-red	Grey-green, then yellow-brown	Blue-red	Red-brown
217	Cibantine Brilliant Green 2GF Tinosol Green 2G Sandozol Green 2G	... Blue	Blue-red	Grey-green, then yellow-brown	Blue-red	Red-brown
217a	Tinon Chlorine Brilliant Green 2GF Sandothrene Brilliant Green N2GF	... Blue	Blue-red	Grey-green, then yellow-brown	Blue-red	Red-brown
217b	Tinon Chlorine Brilliant Green 2G Sandothrene Brilliant Green N2G	... Blue	Blue-red	Grey-green, then yellow-brown	Blue-red	Yellow

TABLE V (contd.)

No.	Dye	Green Dyes			HNO ₃	H ₂ SO ₄	Acid KMnO ₄
		Hydrosulphite					
		Alkaline	Acid				
BLUE (contd.)							
219	Tinon Chlorine Brilliant Green 4G Sandothrene Brilliant Green N4G	...	Blue	Red	Grey-green, then yellow- brown	Red-brown	Yellow
229	Caledon Olive Green B ... Paradone Olive Green B Cibantine Olive 2B Tinosol Olive Green B Sandozol Olive Green B	...	Black-blue	Brown- black	Black- brown (on fibre), returning to green; bleeds green	Green	Brown- yellow
BROWN							
239	Cibanone Khaki 2G ... Tinon Chlorine Khaki 2G Sandothrene Khaki N2G	...	Red-brown	Yellow- green	Brown- green	Black-blue	—
BLACK							
246	Paradone Olive T... Sandothrene Olive NT	...	Black	Yellow- brown	Black-green (on fibre); bleeds red-violet	Green	Brown- yellow

TABLE VI

No.	Dye	Brown Dyes		HNO ₃	H ₂ SO ₄	Acid KMnO ₄		
		Hydrosulphite Alkaline	Acid					
255	Cibantine Brown G	YELLOW				
	Tinosol Brown 2RD			Yellow	Yellow (slowly in heavy dyeings)	Blue		
	Sandozol Brown 2RD							
257	Tinon Chlorine Brown 2B	Yellow	Yellow- brown	Yellow- brown	Violet	—
260	Caledon Dark Brown 3R	Yellow	Brown- green	Red-brown	Green-black	—
	Cibanone Brown BR							
	Cibantine Brown BR							
	Tinon Chlorine Brown BRN							
	Tinosol Brown BR							
	Sandothrene Brown NBR							
	Sandozol Brown BR							
281				BROWN				
	Sandothrene Brown NBG	Brown	Yellow- brown	Yellow- brown	Black-red (on fibre); bleeds red-violet	—

TABLE VII

Grey and Black Dyes								
No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄		
		Alkaline	Acid					
VIOLET								
299	Tinon Chlorine Black BA	Violet	Black-red	Black	Black (on fibre); bleeds black-blue	Brown
BLUE								
307	Caledon Grey 3B ... Caledon Grey 3BP	Blue	Brown-red	Blue-black	Red-violet	Brown-yellow
GREEN								
324	Caledon Grey M ... Paradone Grey M	Blue-green	Black-red	Green-black, then green-blue	Green	Green-yellow

TABLE VII (contd.)

Grey and Black Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
		Alkaline	Acid			
YELLOW						
335	Durindone Printing Black BL ... Ciba Grey BL Cibantine Grey BL Tinon Grey BL Tinosol Grey BL Tetra Grey BL Sandozol Grey BL	Red-yellow	Black-green (stripped)	Black	Black (on fibre); bleeds blue-green	—
BLACK						
343	Cibanone Grey BG ... Tinon Chlorine Grey BG Sandothrene Grey NBG	Red-grey	Brown	Red-black	Yellow-green	Violet-brown

Section II

New Dyes

NOTE

This section includes a few dyes which do not give quite the same colour reactions as their apparent equivalents listed in the original tables. They are, therefore, here treated as new dyes.

Paradone Grey MG, for example, gives the same colour reaction with nitric acid as Paradone Grey M, Caledon Grey M, and Indanthren Grey M (No. 324). It does not, however, give the same colour as Indanthren Grey MG (No. 325), which is said to be a purer form of Indanthren Grey M. It has, therefore, been listed as a new dye.

TABLE I

Yellow and Orange Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
		Alkaline	Acid			
VIOLET						
12a	Caledon Orange 3R	Violet	Brown-yellow	Red-yellow	Red-yellow	—
13b	Caledon Orange 5R	Violet	Brown-yellow	Red-yellow	Red-yellow	—
GREEN						
20a	Caledon Yellow 4G Paradone Yellow 4G	Blue-green	Yellow	Yellow	Red-yellow	—
RED						
39a	Tinon Chlorine Orange 3RE	Brown-red	Yellow	Red-yellow	Red-brown	—
39b	Indigosol Yellow R Tinosol Yellow R	Brown-red	Yellow	Yellow	Yellow	—
39c	Indigosol Golden Yellow AR	Yellow-red	Red-yellow	Red-yellow	Red-yellow	—
BROWN						
45a	Cibanone Golden Orange 2GT Tinon Chlorine Golden Orange 2GT Sandothrene Golden Orange N2GT	Red-brown	Brown-yellow	Red-yellow	Green-yellow	—
45b	Caledon Yellow 2R	Yellow-brown	Brown	Yellow	Yellow-brown, then blue	—
45c	Indanthren Yellow 4GF	Yellow-brown	Yellow-brown	Yellow	Brown-yellow	—
BLACK						
52a	Cibanone Yellow 2GW Tinon Chlorine Yellow 2GW Sandothrene Yellow N2GW	Blue-black	Red-yellow	Yellow	Red-yellow	—
52b	Cibanone Yellow 2GK Sandothrene Yellow N2GK	Blue-black	Yellow	Yellow	Yellow	—
52c	Cibanone Yellow GR	Green-black	Yellow	Yellow	Brown-yellow	—
52d	Indigosol Yellow 2GB Cibantine Yellow 2GB Tinosol Yellow 2GB Sandozol Yellow 2GB	Black	Yellow	Yellow	Red-yellow	—

TABLE VII

Red Dyes

No.	Dye	Hydrosulphite Alkaline	Acid	HNO ₃	H ₂ SO ₄	Acid KMnO ₄
VIOLET						
61a	Caledon Printing Scarlet FR ...	Violet	Red-yellow	Red	Green	—
BLUE						
63a	Cibanone Red 6B... Sandothrene Red N6B	Blue	Blue-red	Green-yellow	Yellow-red	—
63b	Caledon Pink RL...	Green-blue	Red-yellow	Yellow-red	Yellow-red	—
63c	Cibanone Red 2B... Tinon Chlorine Red F4B Sandothrene Red N2B	Green-blue	Red-violet	Green-yellow	Yellow-red	—
GREEN						
66a	Paradone Bordeaux RR ...	Yellow-green	Brown-green	Red-yellow	Yellow-red	—
66b	Cibanone Brilliant Pink G	Blue-green	Red	Red	Red-brown	—
YELLOW						
89a	Durindone Printing Pink 2B Soledon Pink 2B	Green-yellow	Blue-red	Red	Green	—
89b	Indigosol Brilliant Pink I5B Tinosol Brilliant Pink 5B Sandozol Brilliant Pink 5B	Green-yellow	Red	Red	Red (on fibre); bleeds green after a time	—
89c	Indigosol Red AB Tinosol Red AB Sandozol Red AB	Yellow (stripped)	Yellow (stripped)	Red	Blue-green	—
89d	Indigosol Red I2B Tinosol Red 2B Sandozol Red 2B	Green-yellow	Red (stripped)	Red	Green	—
RED						
90a	Caledon Brilliant Red 5B	Black-red	Brown	Blue-red	Brown-yellow	—
BLACK						
103a	Cibanone Brilliant Pink 2R Tinon Chlorine Brilliant Pink 2R Sandothrene Brilliant Pink N2R	Green-black	Red	Red	Grey-red	—
103b	Caledon Red 4B ...	Green-black	Brown	Brown-red	Yellow-red	—
103c	Indanthren Rubine GR ...	Black	Red-brown	Red	Red	—

TABLE III

Violet Dyes

No.	Dye	Hydrosulphite Alkaline	Acid	HNO ₃	H ₂ SO ₄	Acid KMnO ₄
BLUE-RED OR RED-VIOLET						
103d	Indigosol Red Violet IRRL ...	Red-violet	Red-brown	Red-violet, then black-blue	Yellow-green	—
103e	Indigosol Violet I5R ...	Red-violet	Brown	Violet, then black-blue	Yellow-green	—
RED						
120a	Caledon Brilliant Violet 3R ...	Yellow-red	Red-violet	Red-violet	Green	—

TABLE IV

Blue Dyes

No.	Dye		Hydrosulphite Alkaline	Acid	HNO ₃	H ₂ SO ₄	Acid KMnO ₄
VIOLET							
135a	Caledon Dark Blue 2R	Violet	Brown-red	Red-black	Red-violet	Yellow-brown
135b	Indanthren Blue CLB	Violet	Grey-blue	Blue	Yellow	Green-blue
135c	Paradone Dark Blue 58321	Violet	Brown-red	Red-black	Red-violet	Brown-yellow
BLUE							
170a	Sandothrene Blue NGW	Blue	Blue	Green, then yellow	Green-brown	Green-blue
170b	Sandothrene Blue NG40	Blue	Blue	Green, then yellow	Green-brown	Green-blue
170c	Sandothrene Blue NG50	Blue	Blue	Green, then yellow	Green-brown	Green-blue
170d	Sandothrene Blue NGR	Blue	Blue	Green, then yellow	Green-brown	Green-blue
170e	Indanthren Cyanine B	Blue	Blue-red	Green, then black	Blue-red	Yellow-red
170f	Indanthren Navy Blue RB	Blue	Violet	Blue	Black; bleeds violet	Grey-blue
170g	Indanthren Blue GCN	Blue	Blue	Yellow	Green-brown	Green
170h	Indanthren Blue 3GN	Blue	Blue	Yellow	Green-brown	Green-yellow
170j	Paradone Dark Blue RFW	Green-blue	Red-violet	Black-blue	Red-violet	—
170k	Indanthren Navy Blue RN	Green-blue	Violet	Black-blue	Black	Grey-green
BLACK							
207a	Indanthren Dark Blue DB	Blue-black	Brown-black	Brown-green	Black (on fibre); bleeds violet	Brown-green

TABLE V

Green Dyes

No.	Dye		Hydrosulphite Alkaline	Acid	HNO ₃	H ₂ SO ₄	Acid KMnO ₄
BLUE							
232a	Caledon Printing Green 6B	Blue	Blue-red	Green-black	Red-black	Yellow-brown-green
232b	Paradone Jade Green BX	Blue	Blue-red	Grey-green, then yellow-brown	Blue-red	Brown
232c	Tinon Chlorine Green BN	Blue	Blue-red	Brown-green	Black-brown	Brown-yellow
232d	Indigosol Olive Green IMU Tinosol Olive Green 2B Cibantine Olive F2B	...	Black-blue	Black	Black-brown	Green	Brown-yellow
GREEN							
233a	Caledon Olive GL	Green	Brown-green	Black-green	Green-brown	Completely stripped
233b	Cibanone Khaki GR Tinon Khaki GR Tetra Olive NGR	...	Green	Brown-green	Green-black	Brown-green	Yellow (largely stripped)
233c	Caledon Olive MW Indanthren Olive MW	...	Black-green	Green	Green	Green-black	Brown-yellow

TABLE V (contd.)

Green Dyes

No.	Dye			Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
				Alkaline	Acid			
				YELLOW				
235a	Soledon Brilliant Green 3G	Yellow	Yellow	Green	Blue, then brown	Completely stripped
				BROWN				
243a	Indanthren Olive GRL...	Yellow- brown	Grey-green	Grey	Red-violet	Green-grey
243b	Caledon Green 7G	Violet- brown	Red-brown	Green	Yellow- brown	Yellow- green (largely stripped)
				BLACK				
246a	Soledon Olive D...	Violet-black	Grey	Grey, then violet- grey	Blue-green	Yellow (largely stripped)
246b	Caledon Olive D...	Grey	Brown	Brown- green	Green	Yellow
246c	Cibanone Olive S Tinon Chlorine Olive S	Black	Green-black	Green, then red-violet	Green	Yellow

TABLE VI

Brown Dyes

No.	Dye			Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄
				Alkaline	Acid			
				VIOLET				
250a	Indanthren Maroon BR	Black-violet	Red-brown	Black-red-brown	Blue-black	—
				GREEN				
254a	Cibanone Brown 2BR Tinon Chlorine Brown 2BR Sandothrene Brown N2BR	Black-green	Brown-green	Brown	Black (on fibre); bleeds green	—
				RED				
272a	Caledon Dark Brown 2G	Brown-red	Yellow-brown	Brown	Red-brown	—
272b	Cibanone Yellow Brown G Tinon Chlorine Yellow Brown G Sandothrene Yellow Brown NG Sandozol Yellow Brown GL	Brown-red	Yellow-brown	Brown-green	Black-green (on fibre); bleeds green-blue	—
272c	Cibanone Red Brown R Tinon Chlorine Red Brown R Sandothrene Red Brown NR	Brown-red	Red-brown	Brown-green	Black (on fibre); bleeds blue-black	—
				BROWN				
286a	Indigosol Brown I3B Cibanone Brown 3B Cibantine Brown 3B Tinon Chlorine Brown 3B Tinosol Brown 3B Sandothrene Brown N3B Sandozol Brown 3B	Yellow-brown	Brown	Brown	Black (on fibre); bleeds violet	—
286b	Caledon Orange Brown 2G	Red-brown	Brown	Red-yellow	Red-yellow, then green	—
286c	Caledon Brown 3G	Red-brown	Yellow-brown	Brown	Green	—
286d	Soledon Brown R	Red-brown	Yellow-brown	Yellow-brown	Grey-violet	—
286e	Paradone Printing Brown TM	Red-brown	Yellow-brown	Yellow-brown	Blue-red	—

TABLE VI (contd.)

Brown Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄	
		Alkaline	Acid				
		BROWN (contd.)					
286f	Paradone Printing Brown TMI	...	Red-brown	Yellow-brown	Yellow-brown	Blue-red	—
286g	Indanthren Brown LG	Brown	Brown	Brown	Green-blue	—
286h	Cibanone Brown RV ... Tinon Chlorine Brown RV Sandothrene Brown NRV	...	Brown	Yellow-brown	Red-brown	Green-brown	—
286j	Sandothrene Brown NRF	...	Brown	Red-brown	Brown-red	Black-red	—
286k	Sandothrene Brown NR	...	Brown	Red-brown	Red-brown	Brown	—
286l	Sandothrene Brown NRN	...	Brown	Brown-red	Brown	Brown	—
286m	Tinon Chlorine Brown BX	...	Brown	Yellow-brown	Red-brown	Black-red (on fibre); bleeds red	—
286n	Caledon Printing Brown 4R	...	Black-brown	Brown	Yellow-brown	Violet	—
286p	Paradone Red Brown 5RD	...	Brown	Green-brown	Brown	Brown-green	—

TABLE VII

Grey and Black Dyes

No.	Dye	Hydrosulphite		HNO ₃	H ₂ SO ₄	Acid KMnO ₄		
		Alkaline	Acid					
VIOLET								
299a	Caledon Grey AC	Violet	Brown-red	Grey-brown	Red-violet	Red-brown
299b	Indanthren Grey CL	Violet	Brown	Grey	Yellow	Red-brown
299c	Cibanone Black BAN Tinon Chlorine Black BAN Sandothrene Black NBAN	Violet	Red-brown	Black	Black (on fibre); bleeds blue	Yellow- brown
BLUE								
323a	Cibanone Black DRB Sandothrene Black NDRB	Blue	Black-red	Black- brown	Black (on fibre); bleeds red-violet	Brown
323b	Caledon Printing Black 2R	Green-blue	Black-red	Brown- black	Black (on fibre); bleeds red-violet	Green-brown
GREEN								
330a	Cibanone Grey 2GR Tinon Chlorine Grey 2GR Sandothrene Grey N2GR	Green	Red-black	Blue-black	Green	Red-brown
330b	Paradone Grey MG	Blue-green	Black-red	Green- black, then green-blue	Green	Yellow
330c	Durindone Printing Black G	Black- green	Blue-black	Yellow- brown	Black (on fibre); bleeds violet	Yellow- brown
YELLOW								
337a	Durindone Printing Black TL	Red-yellow	Black- green, then green- yellow	Black	Black (on fibre); bleeds blue- green	—

TABLE VII (contd.)

Grey and Black Dyes

No.	Dye			Hydrosulphite Alkaline	Acid	HNO ₃	H ₂ SO ₄	Acid KMnO ₄
YELLOW, (contd.)								
337b	Durindone Printing Black AN...	...		Brown-yellow	Grey-green-brown	Brown	Black (on fibre); bleeds green-blue	Black-violet
BROWN								
342a	Indigosol Grey I3F Cibantine Grey 3G Tinosol Grey 3F	Brown	Yellow-brown	Brown-black	Brown-black (on fibre); bleeds brown-black	—
BLACK								
345a	Caledon Printing Grey BS	Blue-black	Violet	Blue-black	Red-violet	Brown
345b	Cibanone Grey 2BR	Black	Blue-grey	Grey-green, then grey-violet	Green	Brown-yellow

Appendix I

Colour Reactions of Vat Dyes with Sodium Hydrosulphite plus Sodium Carbonate compared with those produced with Sodium Hydrosulphite plus Caustic Soda

The colour produced by treating the vat-dyed pattern with a solution of sodium hydrosulphite and caustic soda at the boil is in some cases significantly different from that obtained by treating it with a solution of sodium hydrosulphite

and sodium carbonate (soda ash) under the same conditions. Vat dyes which show useful colour differences in these two tests are given in the following table; the reactions with sodium hydrosulphite and caustic soda are included for comparison. The sodium hydrosulphite-sodium carbonate reagent is prepared by dissolving 20 g. sodium hydrosulphite in 500 ml. of a cold solution containing 50 g. sodium carbonate (soda ash) per litre. A small sample of the dyed material is boiled with 5 ml. of the reagent for a few seconds.

No.	Dye	Sodium Hydrosulphite	
		+ NaOH	+ Na ₂ CO ₃
YELLOW AND ORANGE DYES			
8	Caledon Yellow 5GS Paradone Yellow GC Indanthren Yellow GC Algol Yellow GC Algol Yellow GCN Cibanone Yellow GC Tiron Yellow 3GF Sandothrene Yellow NGC	Violet	Red
13	Indanthren Orange F3R	Black-violet	Brown-violet
13a	Caledon Orange 3R	Violet	Brown-red
13b	Caledon Orange 5R	Violet	Brown-red
19	Paradone Yellow 2G Indanthren Yellow 3GF	Grey-green	Grey-violet
20a	Caledon Yellow 4G Paradone Yellow 4G	Blue-green	Grey-violet
25	Indanthren Yellow FFRK	Red-yellow	Yellow
28	Caledon Yellow 3R Soledon Yellow 3R Indanthren Yellow 3R Cibanone Yellow 3R Cibanone Yellow 3RF Tiron Chlorine Yellow 3R Tiron Chlorine Yellow 3RN Sandothrene Yellow N3R	Yellow-red	Brown-yellow
29	Paradone Yellow 3RT Indanthren Yellow 3RT	Yellow-red	Brown-yellow

No.	Dye	Sodium Hydrosulphite	
		+ NaOH	+ Na ₂ CO ₃
YELLOW AND ORANGE DYES (contd.)			
39	Caledon Yellow 5GK	Black-red	Red
	Soledon Yellow 5G		
	Paradone Yellow 5GK		
	Indanthren Yellow 5GK		
	Indanthren Yellow 5GK Suprafix		
	Indigosol Yellow V		
	Cibanone Yellow 5GK		
	Cibantine Yellow V		
	Tinon Chlorine Yellow 5GK		
	Tinosol Yellow V		
	Sandothrene Yellow N5GK		
	Sandozol Yellow V		
52a	Cibanone Yellow 2GW	Blue-black	Grey-violet
	Tinon Chlorine Yellow 2GW		
	Sandothrene Yellow N2GW		
52b	Cibanone Yellow 2GK	Blue-black	Yellow-brown
	Sandothrene Yellow N2GK		
52c	Cibanone Yellow GR	Green-black	Grey-red
RED DYES			
54	Caledon Red BN	Grey-blue-red	Brown-red
	Indanthren Red RK		
	Cibanone Red RK		
	Tinon Red RK		
	Sandothrene Red N2R		
58	Indanthren Pink FBBL	Red-violet	Brown-red
61	Caledon Red Violet 2RNS	Violet	Red
	Indanthren Red Violet 2RK		
	Tinon Chlorine Red Violet 2RN		
	Sandothrene Red Violet E2RN		
63c	Cibanone Red 2B	Green-blue	Blue
	Tinon Chlorine Red F4B		
	Sandothrene Red N2B		
101	Indanthren Brilliant Scarlet FR Suprafix ...	Brown-black	Brown
102	Indanthren Scarlet F3G Suprafix	Brown-black	Brown
103	Caledon Brilliant Red 3B	Brown-black	Black-red
	Soledon Red 2B		
	Indanthren Red FBB		
	Indigosol Red IFBB		
	Cibanone Red FBB		
	Cibantine Red FBB		
	Tinon Chlorine Red F2B		
	Tinosol Red F2B		
	Sandothrene Red NF2B		
	Sandozol Red F2B		
103b	Caledon Red 4B	Green-black	Brown
103c	Indanthren Rubine GR	Black	Brown
GREEN DYES			
225	Algol Brilliant Green 5G	Blue	Violet
	Cibanone Green 5G		
	Tinon Chlorine Green 5G		
239	Caledon Khaki 2G	Red-brown	Grey-green
	Indanthren Khaki 2G		
	Cibanone Khaki 2G		
	Tinon Chlorine Khaki 2G		
	Sandothrene Khaki N2G		
246b	Caledon Olive D	Grey	Blue

No.	Dye	Sodium Hydrosulphite			
		+ NaOH	+ Na ₂ CO ₃		
BROWN DYES					
248	Indanthren Red Brown R	Red-violet	Brown-red	
249	Indanthren Brown 3R	Violet	Violet-brown	
273	Indanthren Brown GR	Yellow-brown	Green-brown	
274	Indanthren Brown 3GT	Green-brown	Red-brown	
285	Caledon Dark Brown 4RB	Black	Red-brown	
GREY AND BLACK DYES					
323a	Cibanone Black DRB	Blue	Black-red	
	Sandothrene Black NDRB				
337b	Durindone Printing Black AN	Brown-yellow	Black-green	
342a	Indigosol Grey I3F	Brown	Green-brown	
	Cibantine Grey 3G				
	Tinosol Grey 3F				
343	Indanthren Grey BG	Red-grey	Red	
	Cibanone Grey BG				
	Tinox Chlorine Grey BG				
	Sandothrene Grey NBG				

Index

Name of Dye	Section and No.	Name of Dye	Section and No.
Alizaranthrene Navy Blue RT (ICI)...	I 143	Cibanone (Ciba)—	
Caledon (ICI)—		Black BAN	II 299c
Brilliant Red 3B	I 103	Black DRB	II 323a
Brilliant Red 5B	II 90a	Brilliant Blue R	I 149
Brilliant Violet 3B	I 106a	Brilliant Orange GK	I 9
Brilliant Violet 3R	II 126a	Brilliant Orange RK	I 10
Brown 3G	II 286c	Brilliant Pink G	II 66b
Dark Blue 2R	II 135a	Brilliant Pink 2R	II 103a
Dark Brown 3R	I 260	Brown 3B	II 286a
Dark Brown 2G	II 272a	Brown BR	I 260
Golden Yellow GK	I 31	Brown 2BR	II 254a
Green 7G	II 243b	Brown RV	II 286b
Grey AC	II 290a	Golden Orange 2GT	II 45a
Grey 3B	I 307	Golden Orange 3G	I 42
Grey 3BP	I 307	Golden Yellow GK	I 31
Grey M	I 324	Golden Yellow RK	I 1
Olive D	II 246b	Grey BG	I 343
Olive GL	II 233a	Grey 2BR	II 345a
Olive MW	II 233c	Grey 2GR	II 330a
Olive Green B	I 229	Khaki 2G	I 239
Orange 3R	II 13a	Khaki GR	II 233b
Orange 5R	II 13b	Olive S	II 246c
Orange Brown 2G	II 286b	Red 2B	I 63c
Printing Black 2R	II 323b	Red 6B	II 63a
Printing Brown 4R	II 286n	Red FBB	I 103
Printing Green 6B	II 232a	Red Brown R	II 272c
Printing Grey B	II 345a	Yellow 2GK	II 52b
Printing Scarlet FR	II 61a	Yellow 5GK	I 39
Printing Yellow 6G	I 41	Yellow GR	II 52c
Pink RL	II 63b	Yellow 2GW	II 52a
Red 4B	II 103b	Yellow 3RF	I 28
Yellow 4G	II 20a	Yellow Brown G	II 272b
Yellow 2R	II 45b	Cibantine (Ciba)—	
Yellow 3R	I 28	Blue 2B	I 188
Ciba Grey BL (Ciba)	I 335	Blue 2G	I 185
		Blue GF	I 163

Index (contd.)

Name of Dye	Section and No.	Name of Dye	Section and No.
Cibantine (Ciba) (contd.)—		Indigosol (DH) (contd.)—	
Bordeaux 2RN ...	I 86	Violet 15R ...	II 103e
Brilliant Green BF ...	I 214	Yellow 2GB ...	II 52d
Brilliant Green 2GF ...	I 217	Yellow GC ...	I 8
Brilliant Orange RK ...	I 10	Yellow R ...	II 39b
Brilliant Pink 3B ...	I 82	Paradone (LBH)—	
Brilliant Pink R ...	I 76	Blue Green FFB ...	I 168
Brilliant Pink 2BG ...	I 74	Bordeaux RR ...	II 66a
Brilliant Violet 4R ...	I 109	Brilliant Blue 3G ...	I 146
Brown 3B ...	II 286a	Brilliant Blue R ...	I 149
Brown BR ...	I 260	Brilliant Orange GR ...	I 18
Brown G ...	I 255	Brilliant Orange RK ...	I 10
Golden Orange 2R ...	I 6	Brilliant Pink R ...	I 76
Golden Yellow GK ...	I 31	Brilliant Scarlet RK ...	I 89
Golden Yellow RK ...	I 1	Brilliant Violet 3B ...	I 106
Grey BL ...	I 335	Brilliant Violet 4R ...	I 109
Grey 3G ...	II 342a	Dark Blue 58321 ...	II 170a
Olive 2B ...	I 229	Dark Blue RFW ...	II 170f
Olive F2B ...	II 232d	Golden Yellow GK ...	I 31
Orange R ...	I 21	Golden Yellow RK ...	I 1
Orange 8R ...	I 4	Grey M ...	I 324
Red 3BN ...	I 73	Grey MG ...	II 330b
Red FBB ...	I 103	Jade Green BX ...	II 232b
Scarlet 2B ...	I 78	Navy Blue G ...	I 137
Scarlet 3B ...	I 67	Navy Blue R ...	I 142
Violet 6R ...	I 123	Olive Green B ...	I 229
Yellow 2GB ...	II 52d	Olive T ...	I 246
Yellow V ...	I 39	Orange RRT ...	I 6
Durindone (ICI)—		Printing Brown TM ...	II 286e
Printing Black BL ...	I 335	Printing Brown TMI ...	II 286f
Printing Black AN ...	II 337b	Red Brown 5RD ...	II 286p
Printing Black G ...	II 330c	Scarlet 2G ...	I 64
Printing Black TL ...	II 337a	Scarlet GK ...	I 60
Printing Magenta B ...	I 81	Yellow 4G ...	II 20a
Printing Pink 2B ...	II 89a	Yellow 3RT ...	I 29
Indanthren (BASF, etc.)—		Sandothrene (S)—	
Blue CLB ...	II 135b	Black NBAN ...	II 299c
Blue GCN ...	II 170g	Black NDRB ...	II 323a
Blue 3GN ...	II 170h	Blue NG40 ...	II 170b
Brilliant Green 3B ...	I 215	Blue NG50 ...	II 170c
Brown LG ...	I 286c	Blue NGR ...	II 170d
Cyanine B ...	II 170e	Blue NGW ...	II 170a
Dark Blue DB ...	II 207a	Brilliant Green N2B ...	I 215
Grey CL ...	II 299b	Brilliant Green NBF ...	I 214
Maroon BR ...	II 250a	Brilliant Green N2G ...	I 217b
Navy Blue RB ...	II 170f	Brilliant Green N4G ...	I 219
Navy Blue RN ...	II 170k	Brilliant Green N2GF ...	I 217a
Olive GRL ...	II 243a	Brilliant Pink 2B ...	I 83
Olive MW ...	II 233c	Brilliant Pink N2R ...	II 103a
Rubine GR ...	II 103c	Brilliant Orange NGK ...	I 9
Yellow 4GF ...	II 45c	Brilliant Orange NRK ...	I 10
Indigo 2R (ICI)		Brown N2BR ...	II 54a
Indigosol (DH)—		Brown N3B ...	II 286a
Bordeaux 12RN ...	I 86	Brown NBG ...	I 281
Brilliant Pink 15B ...	II 89b	Brown NBR ...	I 260
Brown 13B ...	II 286a	Brown NR ...	II 286k
Golden Orange 12R ...	I 6	Brown NRF ...	II 286j
Golden Yellow AR ...	II 39c	Brown NRN ...	II 286l
Grey 13F ...	II 342a	Brown NRV ...	II 286h
Olive Green IBU ...	II 232d	Dark Blue NMB ...	I 134
Orange 18R ...	I 4	Golden Orange N3G ...	I 42
Red AB ...	II 89c	Golden Orange N2GT ...	II 45a
Red 12B ...	II 89d	Golden Yellow NGK ...	I 31
Red Violet IRRL ...	II 103d	Golden Yellow NRK ...	I 1
		Grey NBG ...	I 343

Index (contd.)

Name of Dye	Section and No.	Name of Dye	Section and No.
Sandothrene (S) (contd.)—		Tinon Chlorine (Gy)—	
Grey N2GR	II 330a	Black BA	I 299
Khaki N2G	I 239	Black BAN	II 299c
Olive NT	I 246	Brilliant Green 2B	I 215
Red N2B	II 63c	Brilliant Green BF	I 214
Red N6B	II 63a	Brilliant Green 2G	I 217b
Red NF2B	I 103	Brilliant Green 4G	I 219
Red Brown NR	II 272c	Brilliant Green 2GF	I 217a
Violet N2RB	I 108	Brilliant Orange GK	I 9
Yellow NGKF	I 46	Brilliant Orange RK	I 10
Yellow N2GK	II 52b	Brilliant Pink 2R	II 103a
Yellow N5GK	I 39	Brown 2B	I 257
Yellow N2GW	II 52a	Brown 3B	II 286a
Yellow Brown NG	II 272b	Brown BRN	I 260
Sandozol (S)—		Brown BX	II 286a
Blue BC	I 159	Brown 2BR	II 254a
Blue O4B	I 188	Brown RV	II 286b
Bordeaux 2RN	I 86	Dark Blue BOA	I 130
Brilliant Orange RK	I 10	Dark Blue MBA	I 133
Brilliant Pink 5B	II 89b	Golden Orange 3G	I 42
Pink R	I 76	Golden Orange 2GT	II 45a
Brilliant Violet 4R	I 109	Golden Orange 2R	I 6
Brown 3B	II 286a	Golden Yellow GK	I 31
Brown BR	I 260	Golden Yellow RK	I 1
Brown 2RD	I 255	Green BN	II 232c
Golden Orange 2R	I 6	Grey BG	I 343
Golden Yellow GK	I 31	Grey 2GR	II 330a
Golden Yellow RK	I 1	Khaki 2G	I 239
Green B	I 214	Olive S	II 246c
Green 2G	I 217	Orange 3RE	II 39a
Grey BL	I 335	Red F2B	I 103
Olive Green B	I 229	Red F4B	II 63c
Orange R	I 21	Red Brown R	II 272c
Orange 8R	I 4	Rubine R	I 63
Printing Purple R	I 123	Yellow 5GK	I 39
Red AB	II 89c	Yellow GKN	I 46
Red 2B	II 89d	Yellow 2GW	II 52a
Red F2B	I 103	Yellow 3RN	I 28
Red Violet RH	I 73	Yellow Brown G	II 272b
Scarlet B	I 78	Tinosol (Gy)—	
Scarlet 2B	I 67	Blue BC	I 159
Yellow 2GB	II 52d	Blue O4B	I 188
Yellow V	I 39	Bordeaux 2RN	I 86
Yellow Brown GL	II 272b	Brilliant Orange RK	I 10
Soledon (ICI)—		Brilliant Pink 3B	I 82
Brilliant Green 3G	II 235a	Brilliant Pink 5B	II 89b
Brown R	II 286d	Brown 3B	II 286a
Olive D	II 246a	Brown BR	I 260
Pink 2B	II 89a	Brown 2RD	I 255
Yellow 3R	I 28	Golden Orange 2RL	I 6
Tetra (S)—		Golden Yellow GK	I 31
Grey BL	I 335	Golden Yellow RK	I 1
Olive NGR	II 233b	Green B	I 214
Scarlet 2B	I 79	Green 2G	I 217
Tinon (Gy)—		Grey BL	I 335
Bordeaux 2B	I 92	Grey 3F	II 342a
Bordeaux 2RN	I 86	Olive Green B	I 229
Brilliant Pink B	I 77	Olive Green 2B	II 232d
Brilliant Pink R	I 76	Orange R	I 21
Grey BL	I 335	Pink R	I 76
Khaki GR	II 233b	Red AB	II 89c

Index (contd.)				
Name of Dye			Section and No.	
Tinosol (Gy) (contd.)—				
Red 2B	II 89d
Red F2B	I 103
Red Violet RH	I 73
Scarlet B	I 78
Scarlet 3BL	I 67
Yellow CG	I 22
Yellow 2GB	II 52d
Yellow R	II 39b
Yellow V	I 39

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Polarographic Investigation of Fur Dyes and their Oxidation Products

G. SANDBERG

The effect of pH on the oxidation of *p*-phenylenediamine has been investigated. It has been found that the maximum yield of one of the oxidation products—benzoquinone-1:4-bis-(2:5-diaminoanil)—is obtained in a pH interval at which acidity has a marked effect on the state of aggregation of this compound. A change of pH from 6.0 to 7.3 causes its diffusion coefficient to change from 4.8×10^{-5} to 1.0×10^{-5} sq.cm./sec.

As this pH interval covers that used in technical fur dyeing, even small fluctuations in pH have an intricate effect on the diffusion properties of this oxidation product, and therefore also on fur dyeing. Absorption spectroscopy indicates qualitative differences between oxidation products formed at different pH values. There is equivalence between the shifts of position and changes of shape of the absorption bands and the observed changes in slope of the curves of half-wave potential against pH for the different products.

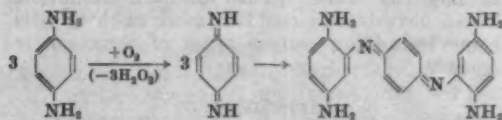
Catalase in the presence of hydrogen peroxide accelerates the oxidative condensation of benzoquinone-1:4-bis-(2:5-diaminoanil). This change can thus be effected very rapidly without applying the usual chromium or copper salts.

Some applications of vertical paper electrophoresis are given, including separation and identification of oxidation products formed under different conditions, and also demonstration of differences between the dissociation constants of different nitro derivatives.

Besides the use of the analytical results in determining the percentages of *p*-phenylenediamine and related compounds in batches from different suppliers, polarography provides a valuable means of determining exhaustion curves in dyebaths, usually comprising a mixture of five or six oxidisable, reducible, and non-reducible substances, where colorimetric methods would meet with difficulties. Hydrogen peroxide, which is always present, is eliminated by the addition of catalase to the different samples of dye liquor.

INTRODUCTION

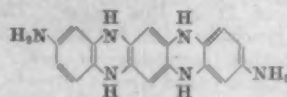
The oxidation products of *p*-phenylenediamine were first independently investigated by Bandrowski¹ and by Erdmann². By the action of oxidising agents in slightly alkaline medium there is formed a compound of empirical formula $C_{12}H_{10}N_4$, corresponding to the quinonediimine $NH:C_6H_4:NH$, which was first prepared by Willstaetter and Mayer³. However, the compound prepared by Bandrowski and by Erdmann has a molecular weight of 318 and is benzoquinone-1:4-bis-(2:5-diaminoanil). Thus, as a preliminary hypothesis, it may be suggested that the reaction proceeds as follows—



The constitution of benzoquinone-1:4-bis-(2:5-diaminoanil) has been confirmed by Heiduschka and Goldstein⁴, Ritter and Schmitz⁵, and Green⁶. Erdmann indicated that about 80% of the compound is formed upon oxidation of *p*-phenylenediamine, but Heiduschka and Goldstein showed that the optimum yield is about 30% of the

theoretical even in the presence of excess of peroxide, some 50% of the diamine remained unchanged, and there was a residue of 20% of unidentified products.

The complications arising in the presence of animal fibres were investigated by Cox⁷, who dyed copper-mordanted rabbit fur and extracted with pyridine the benzoquinone-1:4-bis-(2:5-diaminoanil) formed. After extraction, the fur was found to be strongly dyed, and the dye could be removed only by decomposing the fibre with sodium hydroxide. Cox was not able to ascertain the detailed constitution of the dye, but some of his experiments indicated that the final product is an azine combined with the protein material. Cox was also able to disprove the formula suggested by Austin⁸—



by quantitative reduction to the leuco base. The azine structure requires the grouping—



in which at least one nitrogen is free to form a leuco compound by taking up one hydrogen atom. This is not the case in the formula suggested above.

As previous work has dealt with the oxidation products of *p*-phenylenediamine merely from the preparative point of view, there is still a lack of information upon the following subjects—

(1) Systematic knowledge of the dependence on pH of the quantity and nature of the oxidation products of *p*-phenylenediamine.

(2) The influence of pH on the particle size of the various oxidation products of *p*-phenylenediamine.

(3) The analytical determination of fur dyes and their oxidation products.

These are the main subjects of this investigation, although it seems to be desirable to find out something about catalysts which promote the building-up of higher oxidation products, e.g. the conversion of benzoquinone-1:4-bis-(2:5-diamino-anil) into an azine, under the mild conditions (low temperature, pH near the neutral point) that are generally required in fur dyeing. Some trends in this direction are reported in this paper.

Part I deals with the subjects mentioned above. Part II is concerned with the polarography of some other common fur dyes, all of which are aromatic nitro derivatives, and includes explanatory remarks upon their different polarographic behaviour. Polarography together with spectrophotometry and vertical paper electrophoresis has been the technique generally adopted in this work.

Before going into the experimental details and discussion of the results, it seems desirable to give a brief survey of the fundamental principles of polarography.

GENERAL PRINCIPLES OF POLAROGRAPHY

By applying the general theories of diffusion, Ilkovič⁸ derived the following equation for the diffusion current at the dropping mercury electrode—

$$i_d = 607nD^{1/2}Cm^{1/2}t^{1/2} \quad (i)$$

where n denotes the number of electrons participating in the electrode reaction, D is the diffusion coefficient of the reducible or oxidisable substance (in sq.cm./sec.), C its concentration (in millimoles per litre), m the rate of flow of mercury through the capillary (in mg./sec.), and t the drop time in seconds. Among others, Koutecký¹⁰ has modified equation (i) to give—

$$i_d = 607nD^{1/2}Cm^{1/2}(1 + 34D^{1/2}m^{-1/2}t^{1/2}) \quad (ii)$$

The modified Ilkovič equation has been used in all calculations of D in this paper. The Ilkovič equation is generally valid for any depolarisation process, whether reversible or not, with the exception of the so called kinetic currents, which, in contrast to diffusion currents, are limited by the reaction rate at the electrode surface. In the derivation of equation (i) it is assumed that the limiting current corresponding to a polarographic wave is determined by the rate of diffusion of the reducible or oxidisable substance to the depolarised

electrode. Such a condition exists only if the transport number of the diffusing substance is negligible. An excess of inert electrolyte, the reduction potential of which is far more negative than that of the depolariser, lowers the migration of the diffusing substance practically to zero.

The mathematical expression for the shape of the current-voltage curve is derived from the Nernst equation—

$$E = E_0 + \frac{RT}{nF} \ln \frac{a_{Ox}}{a_{Red}} \quad (iii)$$

The basic equation for the reduction of an organic compound can be represented in simplified form as—



where $Red = OxH_n$ and n varies between 1 and 6 or even more. If the concentrations of the oxidised and reduced forms are substituted in equation (iii), the potential is given according to the Nernst equation by—

$$E = E_0 - \frac{RT}{nF} \ln \frac{[Red]}{[Ox][H^+]^n} \quad (v)$$

where E_0 is the standard redox potential at 25°C. Activity coefficients have been assumed equal to unity and concentrations are those in the immediate vicinity of the electrode. By working in buffered solutions and thus ensuring constancy of $[H^+]$, and by applying the Ilkovič equation, equation (v) is transformed into—

$$E_{d.e.} = E_1 - \frac{0.059}{n} \log \frac{i}{i_d - i} \quad (vi)$$

where E_1 is the half-wave potential at 25°C., i is the current at any point of the wave, and i_d is the diffusion current.

These relationships hold only for reversible electrode reactions of such mobility that the equilibrium state is reached very rapidly in comparison with the drop time.

The number of electrons involved in the Ilkovič equation is usually calculated from known values of D or from coulometric measurements^{11,12} and, at least for reversible systems, n may be estimated from the slope of the curve by using equation (vi).

The expressions for the polarographic currents of various types of electrode process are valid only if the concentration gradients at the electrode are not disturbed by stirring and convection of the electrolyte, which would cause such rapid transport of the depolariser to the surface of the dropping electrode that the current would be several times as large as under normal diffusion conditions. These disturbances could in most cases be overcome by adding various types of surface-active agent¹³.

EXPERIMENTAL

The oxidations of *p*-phenylenediamine were carried out in the Britton-Robinson buffer* containing 50% alcohol in order to determine the optimum pH for the formation of benzoquinone-1:4-bis-(2:5-diaminoanil) and if possible to examine whether other products are formed under different

* 0.08 M-CH₃-COOH + 0.08 M-H₂PO₄ + 0.08 M-H₃BO₃

pH conditions. With m and t of the Ilkovič equation kept constant, and provided that D remains constant in the pH range investigated, it is obviously possible to determine the optimum pH for C_{\max} of benzoquinone-1:4-bis-(2:5-diaminoanil). The general procedure was as follows—

After being oxidised for 24 hr. (initial concentration of *p*-phenylenediamine 0.003 M.) with hydrogen peroxide (0.003 M.), and then freed from oxygen by bubbling purified nitrogen through, the solution was polarographed. After 24 hr. the polarogram consisted of two waves; upon prolonged oxidation (40 hr. or more) three waves had arisen, the hydrogen peroxide wave being included in both cases. Polarograms were determined by means of a Radiometer ink-recording polarograph type PO 3. The capillary had the following characteristics—in the Britton-Robinson buffer of pH = 7.30, at -0.25 v. against the saturated calomel electrode $m = 3.61$ mg./sec. with $t = 2.52$ sec.; $mt^{1/2} = 2.76$ mg./sec.^{1/2}. The electrolysis cell was a jacketed Kalousek vessel with a separate saturated calomel reference electrode. In the case of the experiments with catalase and benzoquinone-1:4-bis-(2:5-diaminoanil) the normal mercurous sulphate electrode was used as reference. The temperature was $25 \pm 0.05^\circ\text{C}$.

The oscillographic measurements were made with a Radiometer oscillograph (Type OSG 32) connected with a square-wave pulse generator and a sine-wave generator of 40–40,000 cycles/sec.

Paper electrophoresis was carried out in the apparatus designed by Durrum¹⁴, which was built in this laboratory, and was fed by 600–800 v. D.C. from a constant-voltage rectifier.

Spectral absorption curves were obtained with a Hilger Uvispek spectrophotometer. From the transmission curves thus obtained, the molar extinction coefficients ϵ were calculated from the equation—

$$\log \frac{I_0}{I} = \epsilon C d \quad (\text{vii})$$

where C is the molar concentration of the substance, d is the thickness of the cell (10 mm.), and I_0 and I are the intensities of the incident and the transmitted light respectively. All absorption curves were obtained at room temperature, about 20 – 21°C . Values of pH were measured by means of a glass electrode. The values measured in the presence of the larger amounts of alcohol must be taken with reservation.

Pure *p*-phenylenediamine (m.p. 138 – 139°C .) was kindly supplied by Messrs. Farbenfabriken Bayer AG., of Leverkusen. It was stored protected from light. Benzoquinone-1:4-bis-(2:5-diaminoanil) (m.p. 238 – 240°C .) was prepared by the method of Ritter and Schmitz⁵.

Calc. for $\text{C}_{12}\text{H}_{10}\text{N}_4$ —

C = 67.90%, H = 5.68%, N = 26.42%

Found—

C = 68.0%, H = 5.7%, N = 26.1% (Dumas).

4-Nitro-1:2-phenylenediamine and 2-nitro-1:4-phenylenediamine were Eastman Kodak products and were recrystallised three times from water; they were dried *in vacuo* (m.p. 196 – 198°C . and 135 – 137°C . respectively).

The catalase was crystalline beef-liver catalase, manufactured by Worthington Biochemical Sales (U.S.A.). Its concentration was determined from the extinction at $622\text{ m}\mu$. in a phosphate buffer of pH 7.1, taking the value 10.8 given by Stern¹⁵ for 0.001 M. catalase in a 10-mm. layer. Four times the value of the extinction coefficient was used according to molecular weight determinations made after the calculations of Stern.

Dioxan was refluxed over sodium for 48 hr. and was distilled twice (b.p. 101°C .).

All other chemicals used were of the conventional analytical grade. In all cases the nitrogen was passed through a wash-bottle containing a solution at the same temperature and of the same composition as that in the cell.

Part I

FIRST WAVE

The first wave was well defined and was attributed to the reduction of benzoquinone-1:4-bis-(2:5-diaminoanil), for this substance was prepared and polarographed in the same pH range as the oxidised *p*-phenylenediamine solution (pH = 2.7 – 10.3). The change in half-wave potential with pH is plotted in Fig. 1, which shows also a plot of the half-wave potential of the anil against pH. The curves are separated by 30 mv. to make the picture clearer. It is seen from Fig. 1 that at pH values below about 5.5 the slope of $E_1 = f(\text{pH})$ of the oxidation product of *p*-phenylenediamine diminishes. An explanation of this will be given in a later section.

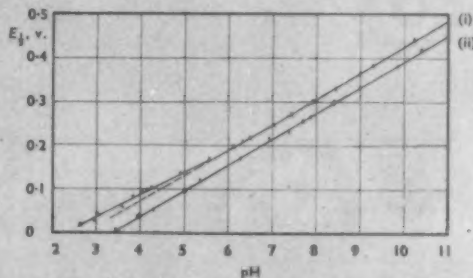


FIG. 1—Dependence of E_1 on pH for the Wave in Oxidised *p*-Phenylenediamine Solution (i) and for Benzoquinone-1:4-bis-(2:5-diaminoanil) (ii)

The half-wave potential* of benzoquinone-1:4-bis-(2:5-diaminoanil) varies with pH according to—

$$E_1 = 0.167 - 0.059 \text{ pH} \quad (\text{viii})$$

Fig. 2 shows the wave height of the anil as a function of pH in the Britton-Robinson buffer solution containing 46% alcohol and 4% dioxan

* Throughout this paper, values of the half-wave potential E_1 are given with reference to that of the saturated calomel electrode (taken as zero).

(from stock solution). The compound gives a single wave in the pH range investigated. ($C = 4.0 \times 10^{-4}$ M.)

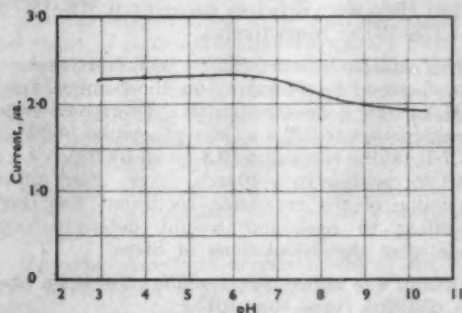


FIG. 2—Dependence of Wave Height on pH for Benzoquinone-1:4-bis-(2:5-diaminoanil)

Fig. 3 shows the dependence of wave height on pH in the oxidised *p*-phenylenediamine solution. It is seen that there is one maximum at pH 8.4 and one at pH 3.2.

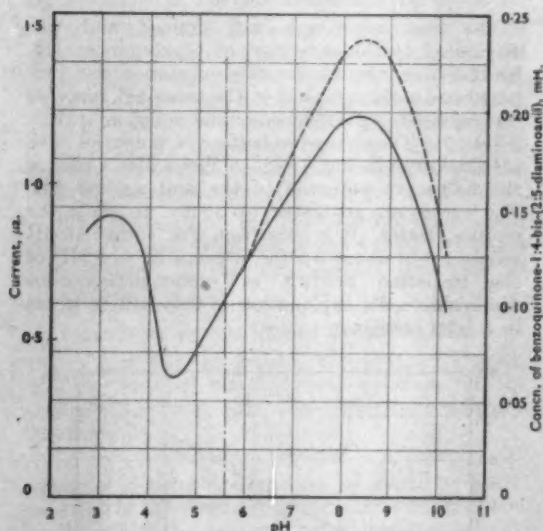


FIG. 3—Wave Height as a Function of pH in Oxidised *p*-Phenylenediamine Solution. Broken curve shows values corrected according to Fig. 2

As appears from Fig. 2, the previous assumption that i_d/C is constant does not hold over the whole pH range. At pH values greater than 7.5 there is a distinct decrease in the diffusion current, which is more marked the less solvent the solution contains. This decrease is probably due to an increase in particle size of the compound, which in turn will cause a diminution in the diffusion coefficient D , and in consequence of this i_d also will have smaller values according to the Ilkovič equation. The diffusion current varies linearly with concentration over the range 10^{-4} – 10^{-3} M. at the different pH values (5.5, 6.7, 8.4, 9.8) investigated. The assumption of increasing aggregation at increasing pH values is confirmed by the following—

(a) To obtain information on the value of n in the electrode reaction, the wave was analysed in detail. The result is shown in Fig. 4, where $E_{d.e.}$ is plotted in the ordinary way against $\log i/(i_d - i)$ at two widely separated pH values, 6.5 and 10.4. The slopes of the two lines are 61 mv. and 36 mv. respectively. Further logarithmic plots at different pH values show an increased deviation from the theoretical slope, 29 mv. for a two-electron process, and a poorer fitting of the points at decreasing pH values.

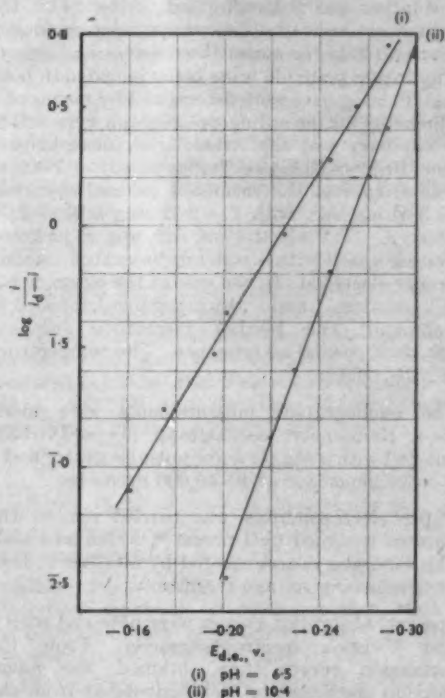


FIG. 4—Plot of $\log i/(i_d - i)$ against $E_{d.e.}$

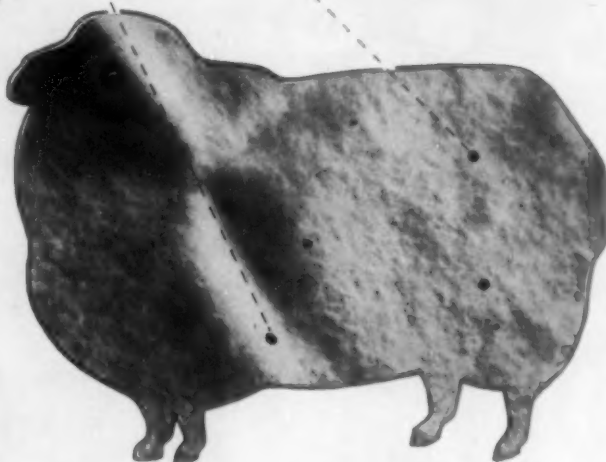
In order to investigate the rate of establishment of equilibrium a streaming mercury electrode was used, together with a cathode-ray oscillograph and the arrangement designed by Heyrovský and Forejt¹⁸. In this the mercury is polarised by an alternating current of 50 cycles/sec. from +0.4 to -2.0 v. and back again. The potential-time curves thus obtained are generally of two types, reversible and irreversible, the reversible type showing a time lag in the presence of a depolariser at the depolarisation potential. This time lag appears at the same potential on the ascending (cathodic) branch as on the descending (anodic) branch. The irreversible type, on the other hand, shows the cathodic and anodic time lags at well separated potentials, or a single time lag on either the anodic or the cathodic branch. To decrease the ohmic drop of potential between the cathode and the anode the concentration of the electrolyte has to be at least normal. Fig. 5 shows the voltage-time curve of benzoquinone-1:4-bis-(2:5-diaminoanil) in N. sodium hydroxide (the compound was injected

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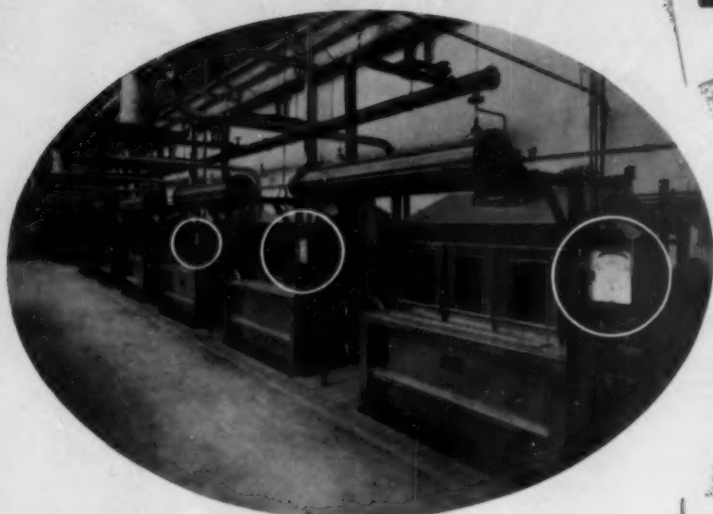
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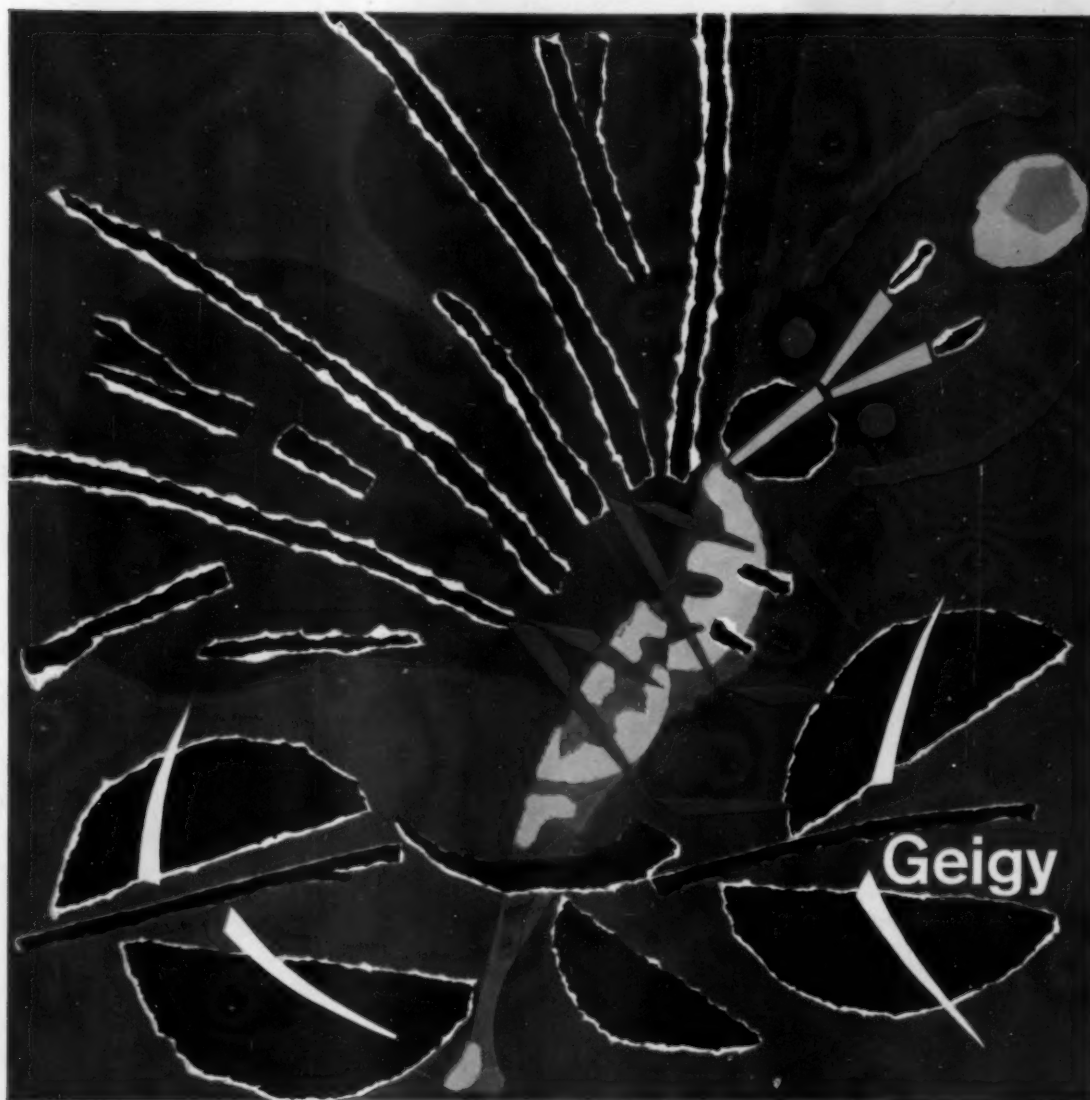
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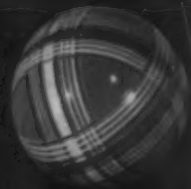
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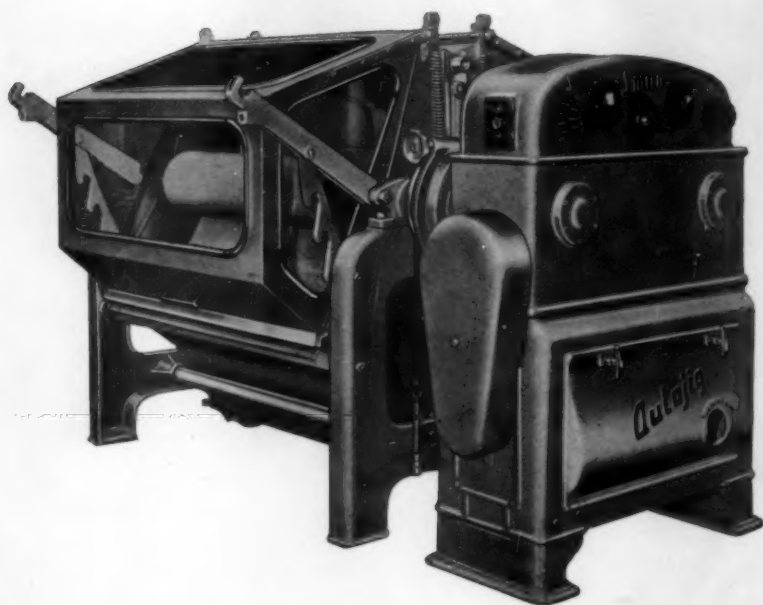
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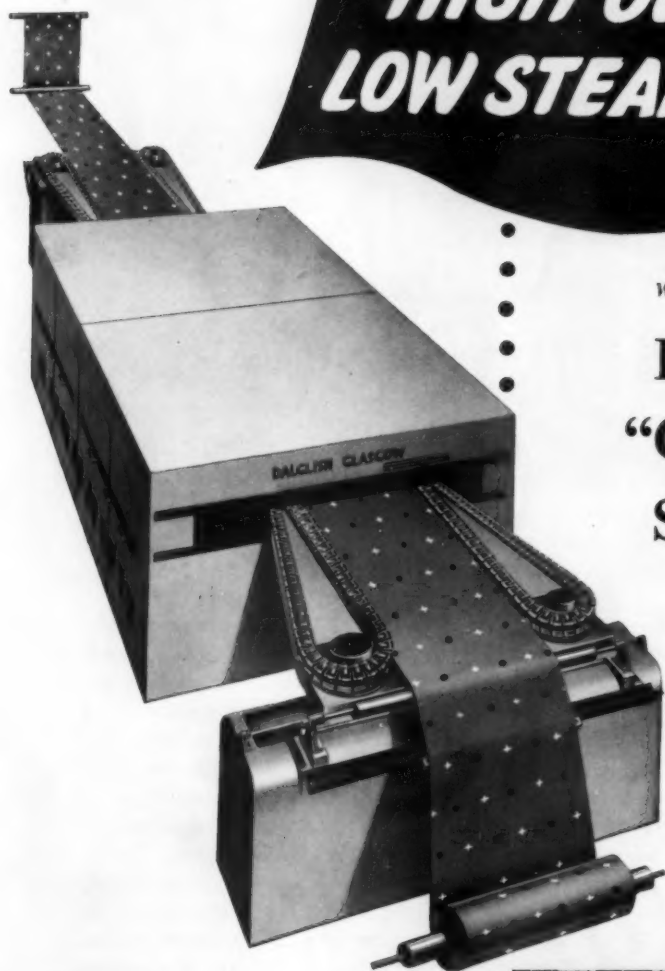
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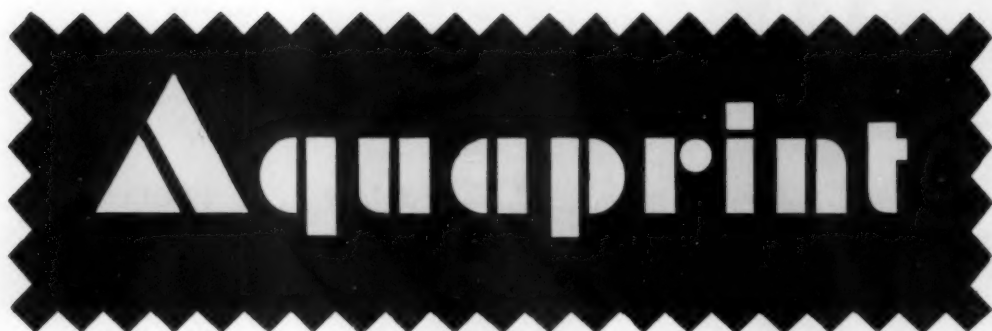
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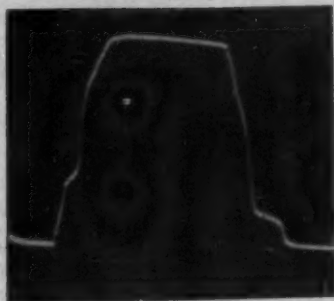
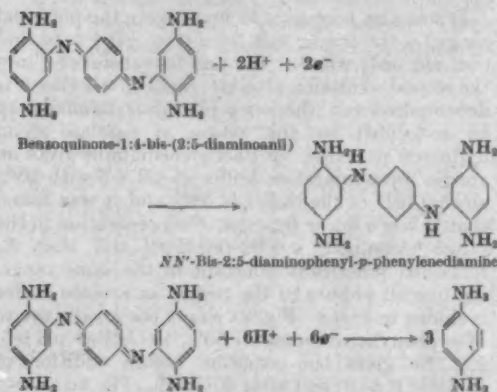


Fig. 5—Oscillographic Voltage-Time Curve of Benzoquinone-1:4-bis-(2:5-diaminoanil) in M. Sodium Hydroxide (streaming mercury electrode, $C = 10^{-3}$ M.)

into the solution, which was stirred with nitrogen; after one minute it precipitated, although this gave enough time to photograph the oscillogram. The time lags corresponding to the depolarisation potentials on the cathodic and anodic branches are reasonably close to each other to meet the requirement of rapid establishment of equilibrium at the mercury electrode. At pH 6.5 in the Britton-Robinson buffer with π . potassium sulphate as inert electrolyte, only a single time lag on the cathodic branch is observed. The results seem to be in good agreement with those obtained in Fig. 4. Of the two possible electrode reactions—



the second possibility must be excluded in accordance with the results mentioned above.

(b) Fig. 6 shows the diffusion currents of the anil at different pH values with different amounts of solvent. The concentration was 4×10^{-4} M., alcohol served as solvent, and the mixtures were prepared from fresh stock solutions of the anil dissolved in dioxan; thus the percentage of solvent indicated in Fig. 6 refers to the total content of alcohol plus dioxan. The Britton-Robinson buffer served as supporting electrolyte, and the analytical concentration of the electrolyte was maintained the same throughout. The rate of flow of mercury through the capillary was measured at the half-wave potential. Diffusion currents were corrected for residual currents. It is seen that there is a distinct difference in the change of the diffusion

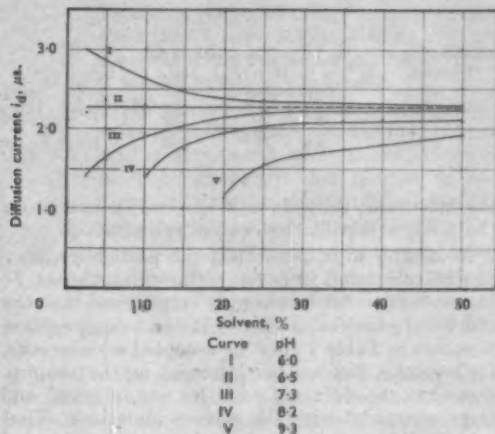


Fig. 6—Diffusion Currents of Benzoquinone-1:4-bis-(2:5-diaminoanil) with Varying Amounts of Solvent at Different pH Values ($C = 4.0 \times 10^{-4}$ M.)

current with decreasing amount of solvent at the different pH values. The possible causes of this seem to be—(1) viscosity effects, (2) aggregation effects, and (3) protolytic effects.

The increase of viscosity η of the medium with increasing amount of solvent up to 50% alcohol will cause the diffusion coefficient D to decrease according to the Stokes-Einstein equation—

$$D = \frac{RT}{N} \cdot \frac{1}{6\pi\eta r} \quad (\text{ix})$$

It should be observed that alcohol-water mixtures have η_{max} at about 45% of alcohol by weight. This seems to be the primary reason for the decrease of i_d with increasing amount of solvent at pH 6 (Curve I).

At pH 7.3 (Curve III) an aggregation effect occurs with an increase of the particle radius r with decreasing amount of solvent and the same decrease of viscosity as at pH 6. There remain the protolytic effects in the two cases. Electrometric titration of the compound in 25% alcohol-dioxan gives a relative $\text{p}K_a$ value of around 7; therefore it is to be expected that at pH 6 the $-\text{NH}_2$ groups will be protolysed to a certain extent, which will hinder aggregation owing to the repulsive electrostatic forces emanating from the $-\text{NH}_3^+$ groups in the molecule. As a result of this, D will increase, and so will i_d . It might also be expected that $\text{p}K_a$ of the anil would increase with decreasing amount of solvent, owing to increase in the dielectric constant of the medium and consequently more pronounced repulsive forces. However, the viscosity and the protolytic effects are hardly distinguishable in this case. At pH 8.2 and 9.3 the $-\text{NH}_2$ groups will be more and more discharged, and the compound will precipitate within a few minutes at lower solvent concentrations than 10 and 20% respectively. Thus the reason for the increased aggregation with increasing pH in 50% solvent solution becomes clearer. It should be noted here that the oscillographic experiments concern the rapidity with which equilibrium is established at

TABLE I

Alcohol + Dioxan (%)	pH = 6.0			pH = 7.3			pH = 8.2		
	<i>D</i> (sq.cm./sec.)	Mol. wt.	<i>a_n</i>	<i>D</i> (sq.cm./sec.)	Mol. wt.	<i>a_n</i>	<i>D</i> (sq.cm./sec.)	Mol. wt.	<i>a_n</i>
10	3.6×10^{-6}	260	1	1.9×10^{-6}	1,900	6	1.0×10^{-6}	13,500	40
2.5	4.8×10^{-6}	350	1	1.0×10^{-6}	38,500	120	—	—	—

the electrode: they do not necessarily indicate a thermodynamically reversible relationship.

According to equation (ix) the particle radius r can be calculated from the diffusion coefficient D . However, it must be strongly emphasised that the order of molecular weights and aggregation numbers in Table I must be accepted with reserve, for equation (ix) has been derived on the assumption that the diffusing particles are spherical and large compared with the solvent molecules. Thus exact validity of equation (ix) is not to be expected in this case. The viscosity values for different solvent concentrations were taken from the Landolt-Börnstein tables¹⁷, the small difference between the viscosities of dioxan and alcohol being neglected. The first column in Table I gives the diffusion coefficient, the second column the order of magnitude of the molecular weight of the particle as calculated from its radius, and finally the third column gives the aggregation factor a_n , i.e. the number of molecules associated to give the calculated molecular weight.

SECOND WAVE

As was mentioned in the experimental section, a second wave occurs, in addition to that corresponding to benzoquinone-1:4-bis-(2:5-diaminoanil), in the oxidised solution of *p*-phenylenediamine. However, the wave could not be observed until the solution had been oxidised for about 40 hr. As the anil gives a single wave in the pH interval investigated, the second wave must emanate from a different product formed in the oxidised solution. Oxidation of *p*-phenylenediamine was carried out in the ordinary way with hydrogen peroxide. After a lapse of 48 hr. a polarogram was taken. In order to eliminate the interference of hydrogen peroxide, the solution was then treated with a dilute catalase solution and bubbled with nitrogen to expel the liberated oxygen. Fig. 7 shows the

polarograms before and after the addition of catalase and also gives the single wave of the anil.

The first wave attains smaller values after the addition of catalase. Identical runs were made with the anil alone and with varying amounts of solvent, catalase, and hydrogen peroxide and in different buffer solutions. After the addition of catalase the wave diminishes and a second wave appears with $E_1 = -0.53$ v. The first wave does not completely disappear, but remains with varying wave height and polarographic characteristics differing from those of the ordinary first wave, at a given time from the catalase addition, depending on different factors.

It seems plausible that the decomposition of hydrogen peroxide by catalase produces oxygen in an activated (atomic) state, which in a comparatively short time promotes the building-up of an oxidation product identical with that formed by prolonged oxidation of *p*-phenylenediamine, as the half-wave potentials coincide.

It was also necessary to investigate the potential range on the anodic side from 0 to +0.4 v. to find out, not only whether the anil is transformed into the second oxidation product, but also whether it is decomposed and whether *p*-phenylenediamine may be re-formed by the action of catalase upon hydrogen peroxide. *p*-Phenylenediamine gives on anodic wave in acetate buffer at pH 6.5 with 50% alcohol (pH of the buffer = 5.6), and it was found that i_d was a linear function of concentration in the range examined, 0.0002–0.002 M., and that E_1 remained practically constant in the same range. An overall picture of the results in acetate buffer is shown in Fig. 8. Fig. 8A shows the anodic waves of *p*-phenylenediamine in 50% alcohol at pH 6.5. Fig. 8B gives the situation before addition of catalase ($t = 0$) and after 65.8 min. Fig. 8C gives a more detailed set of polarograms (to secure more

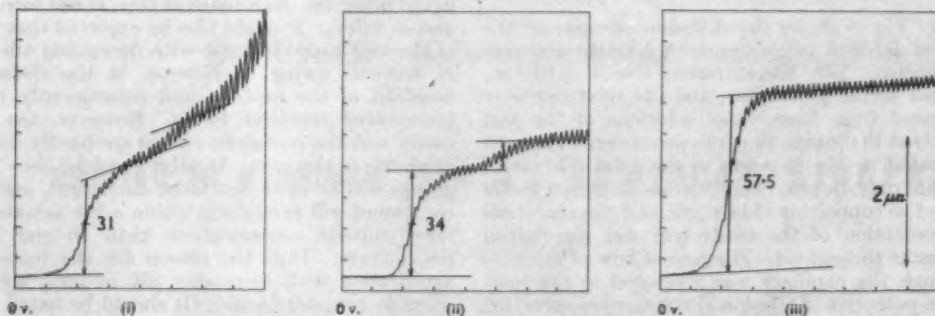


FIG. 7.—Polarograms of Oxidised *p*-Phenylenediamine (i) before and (ii) after Addition of Catalase and (iii) Polarogram of Benzoquinone-1:4-bis-(2:5-diaminoanil) (Catalase concentration in phosphate buffer 10^{-2} M.; accumulator 4 v.; oxidised for 48 hr. pH = 6.5 and sensitivity (S) = 1/150 in all cases)

accurate measurement of the waves, the sensitivity has been changed during the course of the reaction) covering the decomposition of benzoquinone-1:4-bis-(2:5-diaminoanil); the appearance of the second wave is distinctly seen. Finally, Fig. 8D shows the appearance of an anodic wave, which was first thought to emanate from *p*-phenylenediamine. However, the difference in half-wave potential of 44 mv. between the anodic waves in Fig. 8A and Fig. 8D obscures any amine which may be present. Moreover, if the catalase-treated solution is bubbled with oxygen, the anodic wave disappears very rapidly; while in a *p*-phenylenediamine solution, when bubbled with oxygen, the anodic wave remains for days whether the solution contains catalase or not.

The results of these experiments are summarised as follows—

(1) The rate of decomposition of benzoquinone-1:4-bis-(2:5-diaminoanil) depends upon the following factors—

- Hydrogen peroxide concentration
- Catalase concentration
- Catalase strength, as determined by manometric titration
- pH—Optimum value in the neighbourhood of 7
- Nature of Buffer—While Britton-Robinson and acetate buffers behave about the same in this respect, citrate buffer favours the decomposition. Comparable

values of the diffusion current in one experiment are 3.34 μ a. and 2.63 μ a. for acetate and citrate buffers respectively ($t = 40.2$ min.)

- Kind of Solvent—The reaction is markedly retarded by decreasing the alcohol content, and is suppressed when dioxan replaces alcohol. Probably this is due to the decrease in the solubility of the catalase, eventually leading to precipitation.
- Degree of agitation by nitrogen after addition of catalase, i.e. the rate of displacement of dissolved oxygen.
- (2) Reproducibility, after allowing for the above factors, is $\pm 2\%$.

(3) The decomposition curve of the anil and the formation curve of the anodic wave are centrosymmetrical when plotted against time; i.e. there is a close connection between the rate of decomposition of the anil and the rate of formation of the compound indicated by the anodic wave.

From a polarographic point of view, no interpretation of the splitting up of the benzoquinone-1:4-bis-(2:5-diaminoanil) wave into two distinct waves will be given, as the exact nature of the products formed is not known.

ELECTROPHORETIC SEPARATION OF THE OXIDATION PRODUCTS OF *p*-PHENYLENEDIAMINE

In order to get further proof of the existence of different oxidation products of *p*-phenylenediamine, the oxidised solution of the substance was submitted to vertical paper electrophoresis in the

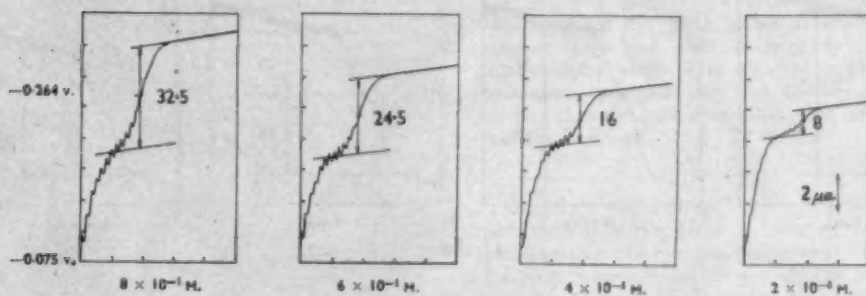


FIG. 8A—Anodic Waves of *p*-Phenylenediamine ($S = 1/500$)

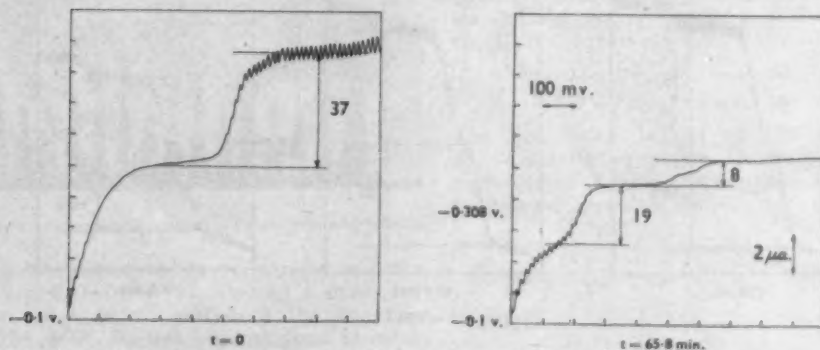


FIG. 8B—Anodic Waves before and after Addition of Catalase ($S = 1/500$)

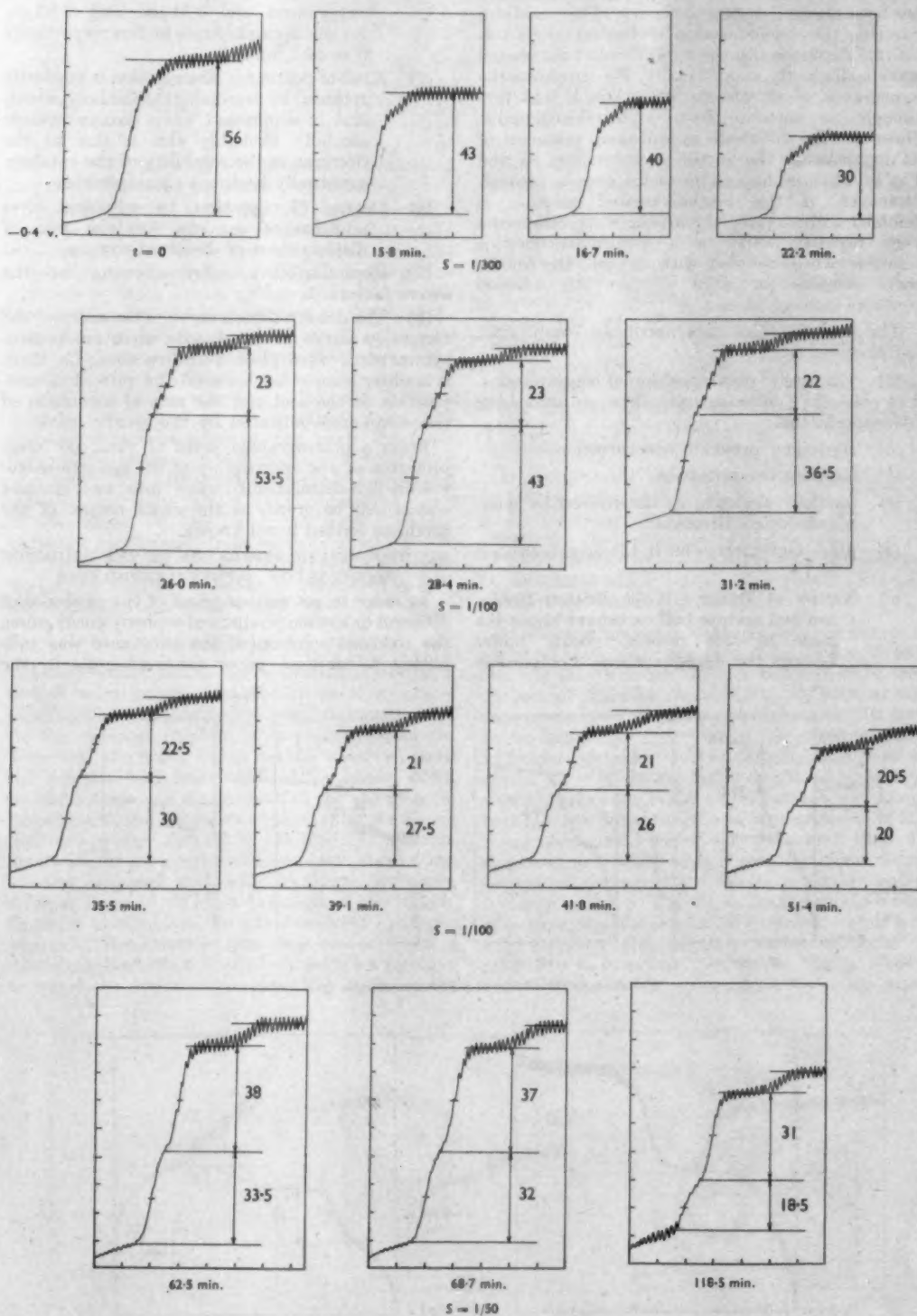


FIG. 8c—Decomposition of Benzoquinone-1:4-bis-(2:5-diaminoanil) ($C = 8.5 \times 10^{-4}M$.)

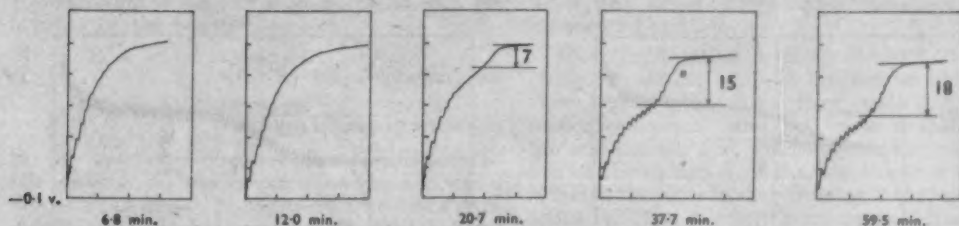
FIG. 8D—Further Anodic Wave ($S = 1/500$)

FIG. 9—Decomposition of Benzoquinone-1:4-bis-(2:5-diaminoanil) by the Action of Catalase on Hydrogen Peroxide (catalase concn. 5×10^{-6} M.; acetate buffer in 4.25% dioxan + 46.75% alcohol; H_2O_2 concn. 1.7×10^{-3} M.; accumulator 6 v.; pH = 6.5)

continuous apparatus described by Durrum¹⁴. Fig. 9 shows a photograph of a curtain resulting from a solution of oxidised *p*-phenylenediamine (oxidation time 48 hr., initial concentrations 0.025 M. *p*-phenylenediamine and 0.025 M. hydrogen peroxide). Britton-Robinson buffer served as background electrolyte with 50% alcohol (pH 6.5, applied voltage 800 v. D.C.). The separation was carried out at $+7^\circ\text{C}$. in order to avoid boiling effects due to the presence of alcohol.

are too close to permit a complete separation. Zone 4 (red) is moving considerably faster than zone 3 (violet) and zone 5 (blue), obviously because of different adsorption on the paper and possibly different particle sizes.

After having been collected, the different fractions were polarographed. The bright red zone gave rise to a wave with a half-wave potential corresponding exactly to that of the second wave mentioned in earlier sections. In none of the other fractions is the presence of benzoquinone-1:4-bis-(2:5-diaminoanil) indicated either by measured half-wave potentials or by the characteristic reactions of this compound.

Part II

INTRODUCTION

The reduction of aromatic nitro compounds at the dropping mercury electrode indicates that in acid medium the nitro group is reduced in two steps to the amine, with the hydroxylamine as the intermediate stage. In alkaline solutions most reductions proceed only to the hydroxylamine stage. However, exceptions to this generalisation frequently occur.

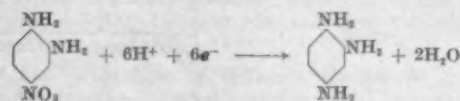
RESULTS

In the pH range 1.81–10.4, 4-nitro-1:2-phenylenediamine gives a single wave corresponding to a six-electron reduction, while 2-nitro-1:4-phenylenediamine gives a double wave in acid medium, the sum of the waves being equal to that of the former compound. The concept of a six-electron reduction was obtained by calculating the diffusion coefficients for $n = 4$ and $n = 6$ in the Ilkovič equation—

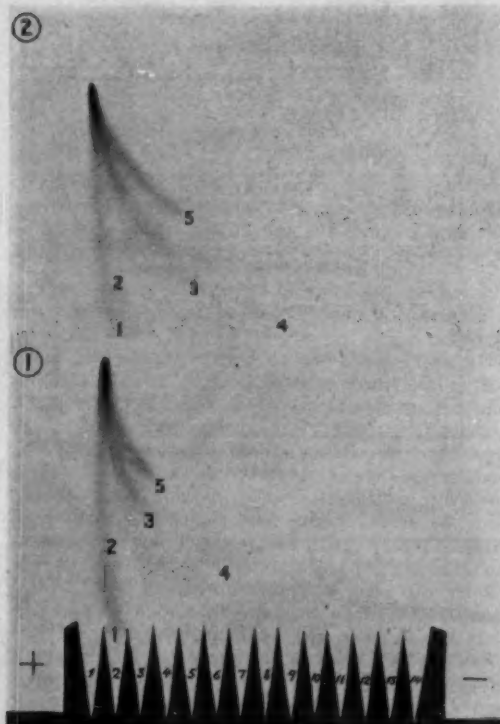
$$n = 4, \quad D = 1.6 \times 10^{-5} \text{ sq.cm./sec.}$$

$$n = 6, \quad D = 7.2 \times 10^{-5} \text{ sq.cm./sec.}$$

The first value is out of the question, of $D_{O_2} = 2 \times 10^{-5} \text{ sq.cm./sec.}$ Generally, the cathodic reduction of 4-nitro-1:2-phenylenediamine seems to proceed according to—



1:2:4-Triaminobenzene

FIG. 9—Electropherograms of Oxidised *p*-Phenylenediamine Solution

Five zones corresponding to various mobility species are visible (Fig. 9). Curtain 1 shows the situation after 10 hr.; curtain 2 the situation after 16 hr., when fraction 1 is just about to reach drip point 2. Zone 1 (yellow) and zone 2 (brown)

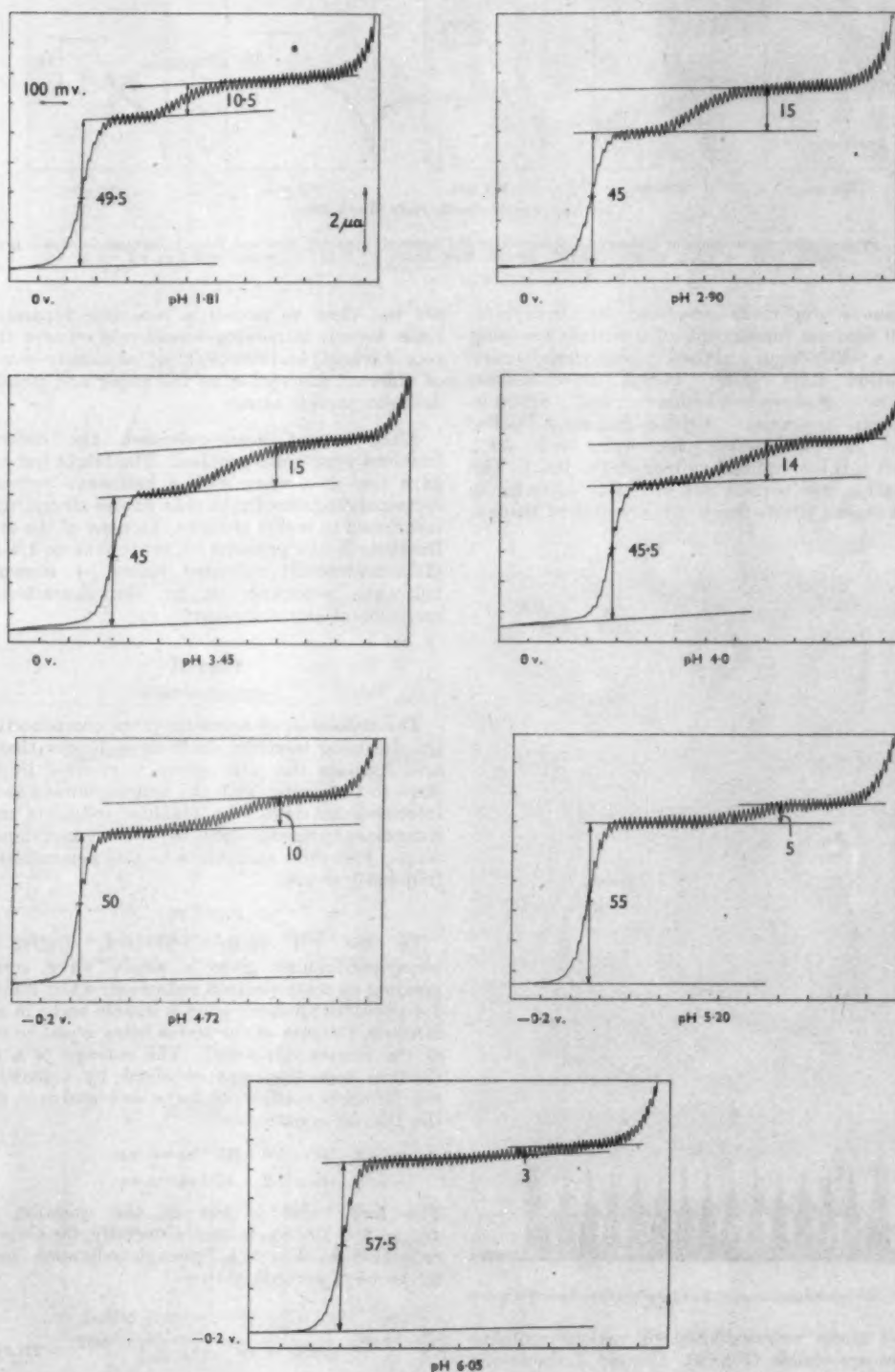


FIG. 10—Polarograms of 2-Nitro-1:4-phenylenediamine in Britton-Robinson Buffer containing 0.006% Gelatin (accumulator 4V; $C = 2 \times 10^{-3} M$; $S = 1/800$)

The variation of the half-wave potential with pH is given by the equation—

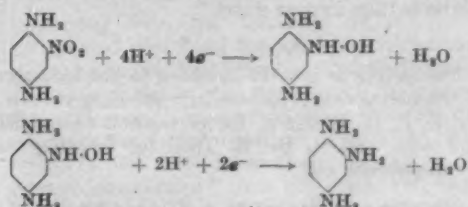
$$E_1 = -0.125 - 0.065 \text{ pH} \quad (2\text{-Nitro-1:4-phenylenediamine})$$

$$E_1 = -0.153 - 0.065 \text{ pH} \quad (4\text{-Nitro-1:2-phenylenediamine})$$

In the case of 2-nitro-1:4-phenylenediamine in acid medium, E_1 was measured on the first wave. The small difference in half-wave potential makes simultaneous determination of the two isomers impossible.

The wave height varies linearly with concentration in the range $0.05\text{--}2.0 \times 10^{-3}$ M. at pH 7.3 with 0.006% gelatin added as peak suppressor.

Fig. 10 shows the split-up of the wave of 2-nitro-1:4-phenylenediamine in the Britton-Robinson buffer. As the sum of the wave heights is exactly the same as the height of the wave of 4-nitro-1:2-phenylenediamine, the total electrode reaction might be considered the same as that represented above, because the end-product, 1:2:4-triaminobenzene, is the same in both cases. A stepwise reduction via the hydroxylamine stage—



requires a ratio between the second and the first waves of 1:2. This is not the case at any pH nor at any concentration in the pH range shown in Fig. 10.

The split-up of the wave seems to be due to the position of the nitro group in the aromatic nucleus, which greatly affects the pK_a values of these compounds, owing to the strongly electrophilic character of the nitro group. While the pK_a (≈ 4.7) of 2-nitro-1:4-phenylenediamine could easily be determined by electrometric titration, this procedure could not be used with sufficient accuracy with 4-nitro-1:2-phenylenediamine, because of its comparatively low solubility in water. The latter compound was submitted to electrophoresis in the Durrum cell with 0.25 M. acetic acid as back electrolyte and an applied potential of 600 v. D.C. For comparison the same procedure was carried out with 2-nitro-1:4-phenylenediamine and *m*- and *p*-nitroaniline ($pK_a = 2.6$ and 1.1 respectively). The angles between the different zones and the vertical then give an indication of the relative dissociation constants of the compounds, the larger the angle the larger the pK_a . The angles of deviation in the experiments were approximately—

2-Nitro-1:4-phenylenediamine	50°
<i>m</i> -Nitroaniline	25°
4-Nitro-1:2-phenylenediamine	18°
<i>p</i> -Nitroaniline	9°

Thus pK_a for 4-nitro-1:2-phenylenediamine lies between 1.1 and 2.6.

According to these determinations, 2-nitro-1:4-phenylenediamine will be ionised at considerably higher pH values than will 4-nitro-1:2-phenylenediamine. This will cause a split-up of the wave of the first compound, one wave being due to the reduction of the undissociated species R-NH_3^+ , the other to the reduction of the unionised amine R-NH_2 . A refined mathematical treatment of the complicated changes in ionic equilibria which occur is beyond the scope of this paper.

Discussion

In Part I it was observed that the slope of the E_1 -pH curve in the oxidised *p*-phenylenediamine solution falls at pH values below about 5.5. Some preparations of the oxidation products of *p*-

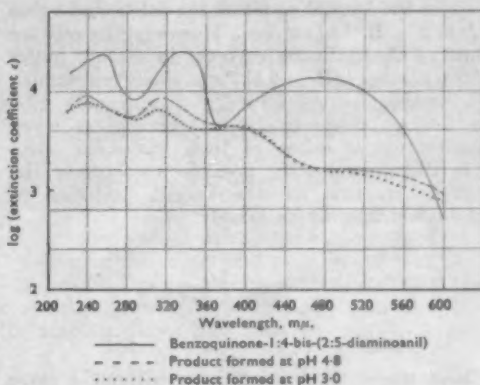
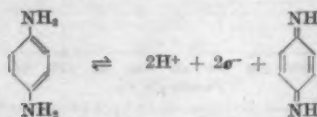


Fig. 11—Absorption Spectra of Compounds formed by Oxidation of *p*-Phenylenediamine at Different pH Values

phenylenediamine were made at pH 3.0 and at pH 4.8. The oxidation products were recrystallised twice from dioxan. They both had melting points above 275°C. The absorption spectra of benzoquinone-1:4-bis-(2:5-diaminoanil) and the oxidation products mentioned above, all dissolved in dioxan, are shown in Fig. 11. While the anil exhibits two distinct bands at 255 and 335 mμ, as well as the broad band typical of aromatic amines, which in this case is at 475 mμ, the bands of the other two compounds show a marked hypsochromic shift to 240 and 308 mμ. The broad band has almost disappeared and there remains a diffuse band at 400 mμ and a doubtful one in the neighbourhood of 540 mμ. From these data it seems quite certain that at lower pH values there are formed products which differ widely in constitution from the anil, and it seems reasonable to believe that the two compounds formed at pH 3.0 and 4.8 are closely related constitutionally. Thus, at lower pH values the E_1 of the wave obtained will include a mixed half-wave potential, especially in the pH range 4.5–6.0, between the anil and the other oxidation products.

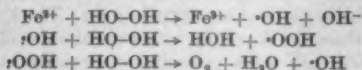
The evaluation of diffusion coefficients from polarographic diffusion currents might be open to criticism, since D as calculated from the Ilkovič

equation will include a quadratic error and, especially with poorly defined residual currents, as, for example, the anodic wave of *p*-phenylenediamine in Fig. 8, large errors will of course be involved because of the difficulty of measuring the true diffusion current. From a strictly polarographic point of view Hans¹⁸ has shed new light on the subject. In the case of the anodic wave of *p*-phenylenediamine the results in 0.4 M. sodium hydroxide in 50% alcohol are the most suitable for analytical purposes, with a very well defined anodic wave. With $C = 4.0 \times 10^{-4}$ M. $i_d = 3.14 \mu\text{A}$., while in acetate buffer (pH 6.5) in 50% alcohol $i_d = 2.5 \mu\text{A}$. In the Britton-Robinson buffer, without solvent, the depolarisation proceeds in a single wave in the pH range 6.50–10.2. However, in 0.2 M. sodium hydroxide the diffusion current is $4.25 \mu\text{A}$. The increase from 3.14 to $4.25 \mu\text{A}$. must originate from the change in viscosity. With $n = 2$ in the Ilkovič equation the calculated value of D is 9×10^{-6} sq.cm./sec. However, the relative values of the diffusion currents in acetate buffer in 50% alcohol (pH = 6.5) for *p*-phenylenediamine and benzoquinone-1:4-bis-(2:5-diaminoanil) (2.5 and $2.32 \mu\text{A}$. respectively) are anomalous when consideration is taken of their molecular sizes. It is therefore hardly possible to express the electrode reaction for the anodic oxidation of *p*-phenylenediamine as simply as—



at least under these conditions, without a more detailed study. In 0.4 M. sodium hydroxide in 50% alcohol i_d is proportional to concentration between 5×10^{-5} and 2×10^{-3} M.

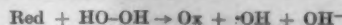
A few remarks should still be made on the catalase-hydrogen peroxide reaction with benzoquinone-1:4-bis-(2:5-diaminoanil). There seems to be no doubt that the compound, formed in the oxidised *p*-phenylenediamine solution, indicated by the second wave in Fig. 7, results either from direct oxidation of the anil or from interaction between the anil and the *p*-phenylenediamine. We are forced to believe that the first reaction is the actual one, because of the results in Fig. 7 and because the second wave arises after about three days or more in solutions of the anil in the presence of hydrogen peroxide, without any detectable formation of anodic waves, which would indicate the presence of *p*-phenylenediamine. Furthermore, the action of catalase on hydrogen peroxide is usually represented by the following chain reactions with formation of free radicals—



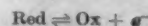
The chain reactions are broken by the process—



This may be generalised into—



where—



The results show the redox character of the system. However, the nature of the depolariser giving rise to the anodic wave in Fig. 8d has not been further investigated.

Finally, it should be noted that the velocity of decomposition of the anil is considerably diminished with low alcohol contents, apart from any effects due to change in pH. On the one hand, owing to the precipitating effect of larger amounts of solvent on catalase, the resonance energy of the catalase molecule will be limited by adsorption; on the other hand, this may slow down the decomposition of hydrogen peroxide, so that the supply of oxygen will become more steady. It should also be emphasised that the solubility of molecular oxygen is greater in alcohol-water mixtures than in pure water.

* * *

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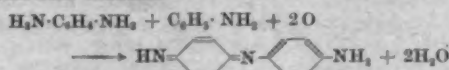
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Detection of Dyes possessing a *p*-Phenylenediamine or a *p*-Nitroaniline Structure by means of Spot Tests

F. FEIGL and C. COSTA NETO*

When Bandrowski's base and azo dyes containing a *p*-phenylenediamine or a *p*-nitroaniline structure are fused with a dry mixture of sodium formate and sodium hydroxide at 210–230°C. *p*-phenylenediamine is formed by reductive cleavage. Under these conditions the diamine sublimes and the vapour reacts with an acetic-acid solution of aniline and alkali-metal persulphate to yield the indamine dye Phenylene Blue. This procedure may be conducted by the technique of spot test analysis and serves to detect such dyes. The detection limits are in the range 5–10 µg., as has been verified by testing thirteen pertinent compounds.

Heim¹ has described a sensitive spot test for *p*-phenylenediamine, the limit of identification of which is 0.5 µg. The test is based on the production of the indamine dye Phenylene Blue (C.I. 818) from the reaction of *p*-phenylenediamine and aniline with alkali-metal persulphate as oxidant in acetic-acid solution—



Reasoning from the behaviour of dimethyl-*p*-phenylenediamine and *p*-toluenediamine sulphate, Heim assumed that compounds containing a *p*-phenylenediamine structure could be detected by analogous colour reactions. However, this generalisation is too broad. For example, Bandrowski's base (I), formed by oxidation from *p*-phenylenediamine², does not react with aniline and persulphate, nor do any of the numerous azo dyes possessing a *p*-phenylenediamine structure. Aminoazobenzene (II) is a pertinent instance.

For practical purposes, the detection of derivatives of *p*-phenylenediamine has more interest than that of the parent compound. Apparently there is no procedure available for the certain and sensitive detection of the presence of Bandrowski's base† in black-dyed furs‡. This problem is obviously of importance, because *p*-phenylenediamine and its oxidation products are poisonous and their use in cosmetics is therefore prohibited. There is, furthermore, a need in dye chemistry for a procedure for detecting azo dyes that have been prepared from *p*-phenylenediamine.

The test described here is based on the occurrence and the utilisation of the following effects—

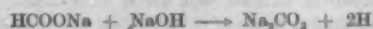
(1) Derivatives of *p*-phenylenediamine are reductively split by nascent hydrogen with liberation of the diamine.

(2) *p*-Phenylenediamine (m.p. 95°C., b.p. 267°C.) sublimes in a stream of hydrogen even below its melting point⁴.

(3) *p*-Phenylenediamine vapour reacts on contact with the Heim reagent.

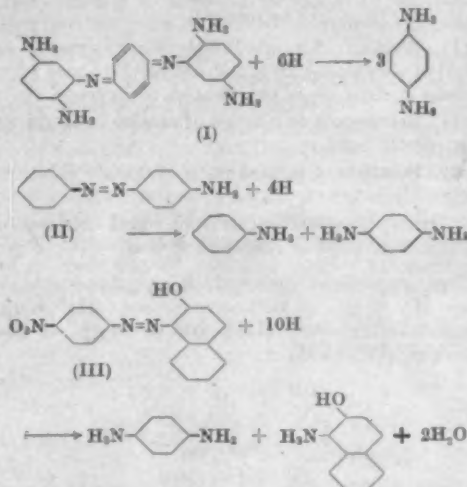
It has been found that (1)–(3) are easily realisable if some of the solid test material is heated

with a dry mixture of sodium formate and sodium hydroxide. Haber and Bruner⁵ found that this mixture decomposes quantitatively when heated to 205°C.—



Consequently, the production of *p*-phenylenediamine here involves the reductive cleavage of its derivatives by the nascent hydrogen furnished by the formate-caustic alkali melt. As anticipated, this formate fusion likewise yielded *p*-diphenylenediamine by reduction and reductive splitting of *p*-nitroaniline—and of azo dyes having a *p*-nitroaniline structure§.

If the partial reactions are disregarded, the following net reactions may be written for the formation of *p*-phenylenediamine from Bandrowski's base (I), *p*-aminoazobenzene (II), and Paranitraniline Red (III)—



§ The release of hydrogen by sodium formate or a sodium formate-hydroxide mixture was first used for analytical purposes by Vourasos⁶, who thus converted arsenic of inorganic and organic compounds into arsenic hydrides. The tests described in the present paper make it likely that fusion reactions with alkali formate will be useful in qualitative organic analysis and perhaps even in preparation methods. It has been found that heating *p*-dinitrobenzene and *p*-nitronitrosobenzene with sodium formate yields *p*-phenylenediamine. Aniline is split off from *p*-hydroxyazobenzene, and hydrochloric acid is liberated from 2:4-dichloromandellic acid and pentachlorophenol. Similarly, sodium formate fusion produces hydrogen bromide and hydrogen iodide from dibromocresolsulphonphthalein and iodohydroxyquinoline sulphonate respectively.⁷

† Communication from the J. Schuster Co., Brooklyn, N.Y.

‡ Erdmann³ found that the brown solution of Bandrowski's base in dilute hydrochloric acid turns red on boiling. Our trials have shown that this test is neither sensitive nor reliable.

* Translated from the German by Professor R. E. Osper, University of Cincinnati, U.S.A.

Analogous reductive cleavages can probably be written for dyes of more complicated structure of the same general classes. With non-fusible dyes or their salts, the reactions patently become topochemical, i.e. the hydrogen formed by the sodium formate-sodium hydroxide mixture reacts only at the surface of the unaltered solid dye, splitting off *p*-phenylenediamine.

Extremely small amounts are sufficient for these fusion reactions. Accordingly, these tests with the solid samples can be conducted by the techniques of spot test analysis⁷ and provide a convenient means of detecting dyes possessing a *p*-phenylenediamine or *p*-nitroaniline structure. As might be expected, benzidine and its derivatives do not react.

PROCEDURE

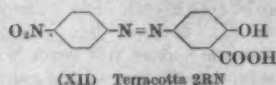
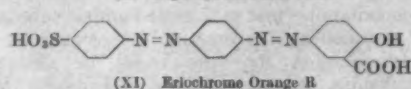
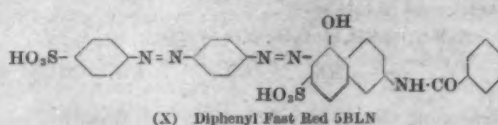
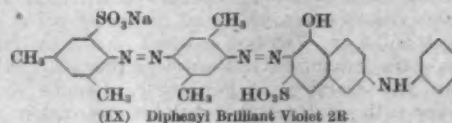
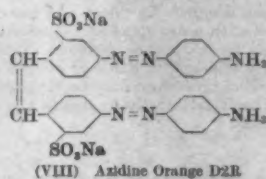
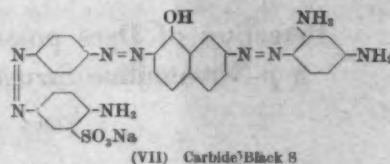
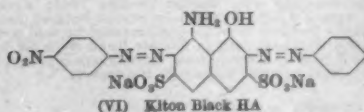
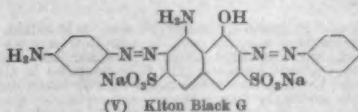
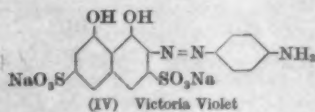
The test is carried out in a micro test tube. Several milligrams of the solid formate-alkali mixture is added to a tiny portion of the solid material being tested. A drop of water is added, and the contents of the tube are stirred and then taken to dryness. If the sample is already in solution, a drop is added to a little of the formate mixture, and the whole taken to dryness. The test tube is then suspended in an oil-bath previously heated to 205°C., and the mouth is covered with a disc of filter paper which has been moistened with a drop of the reagent solution. The temperature is then raised to 210–220°C. Depending on the quantity of *p*-phenylenediamine released, a deep blue to light blue stain appears on the reagent paper either at once or within a few minutes.

REAGENTS

- (1) Sodium formate-hydroxide mixture—a solution containing 20% sodium formate and 12% sodium hydroxide is evaporated to dryness.
- (2) Solution of two drops of aniline in 50 ml. of 10% acetic acid.
- (3) Solution of potassium persulphate in water (2%)

A freshly prepared mixture of equal volumes of (2) and (3) is used as reagent solution.

The procedure detected 9 μg. Bandrowski's base (I), 5 μg. *p*-aminoazobenzene (II), 6 μg. Paranitraniline Red (III), and 5–10 μg. of the azo dyes (IV)–(XII).



Dye IX shows that also nuclearly substituted phenylenediamines, split off by a sodium formate-sodium hydroxide mixture, react in the vapour form. It seems that in this case, too, evaporation (sublimation) is favoured by the hydrogen formed. It is remarkable that *N*-methyl-*p*-phenylenediamine and *NN*-bis-β-hydroxyethyl-*p*-phenylenediamine also give a positive response when heated over a Bunsen burner.

The authors are grateful for the support of this study by the Conselho Nacional de Pesquisas.

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(Received 4th October 1955)

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- ⁴ Beilstein, *Handbuch der organischen Chemie*, **13**, 63 (Berlin 1930).
- ⁵ Haber, F., and Bruner, E., *Z. Elektrochem.*, **10**, 706 (1904).
- ⁶ Vournasos, A. C., *Ber. deutsch. chem. Ges.*, **43**, 2264 (1910).
- ⁷ Cf. Feigl, F., *Spot Tests* (New York: Elsevier Publishing Co. 4th edition 1954).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Effect of Organic Solvents on Wool Dyeing

In a recent letter Stevens and Peters¹ report that the rate of uptake of neutral-dyeing dyes by wool can be greatly accelerated at low temperatures by the addition of alcohols and phenols to the dye liquor.

It may be relevant that some of the effective substances have been found to break up the micelles into which certain dyes aggregate in solution. We showed² that a number of neutral-dyeing dyes exist as units having molecular weights ranging from 10,000 to 50,000 below 60°C., but break down at a higher temperature. The failure of these dyes to penetrate wool within any reasonable time at low temperatures is due to this aggregation. The addition of hydrogen-bond-breaking substances, and in particular phenol, causes these aggregates of some dyes (e.g. Benzopurpurin 4B and Coomassie Milling Scarlet 5B) to break down even at room temperature, while the micelles of the dye Polar Yellow R are not changed^{2,3}.

It would be interesting to know whether this is the only factor responsible for the increase in uptake of dyes at low temperatures on the addition of phenols and the like, or whether these substances affect also the properties of the fibres and thus assist penetration. This point could be decided by comparing the action of a number of substances as dyeing assistants with their ability to decrease the size of dye aggregates.

P. ALEXANDER

K. A. STACEY

17A ONSLOW GARDENS
LONDON S.W.7

28th March 1956

I have read with interest the letter of Stevens and Peters¹, the article by the same authors⁴, and various statements in the daily newspapers.

We would point out that, although this is an interesting development, the use of organic solvents in wool dyeing is not a new discovery, as there already exist patents covering the use of water-soluble alcohols, esters, and aliphatic ketones and emulsions of these products for the low-temperature dyeing of animal fibres^{5,6}.

Dyemakers have not overlooked the importance of this earlier work, and my Company has also taken out provisional patents in Switzerland⁷ covering the use of a number of solvents, which

are in no way related in constitution to those mentioned by Stevens and Peters.

G. H. LISTER

SANDOZ PRODUCTS LTD.
152 CANAL ROAD
BRADFORD 2
YORKSHIRE

4th April 1956

We thank Dr. Alexander and Dr. Stacey for offering an explanation of the phenomena we reported in this *Journal*¹. The account given in the *Dyer*⁴ is not mentioned by them, and we assume that they have not had the opportunity of studying it, as otherwise they would have found it more difficult to reconcile their theory with the additional data given therein.

The Ciba patents to which Dr. Lister refers^{5,6} also appear to aim at either reducing the aggregation or increasing the solubility of the dye in the aqueous phase of the dyebath, an effect which is quite different in principle from our method, and we do not consider that these patents anticipate our discovery.

Since no details of the Sandoz patent application⁷ are given, we cannot usefully comment upon it.

It may be of interest to record that the general principles were arrived at, and our first confirmatory experiments carried out, in August 1954. A further investigation was approved as a suitable topic for a Diploma Thesis by the Department of Textile Industries at Leeds University in October 1954, and the completed thesis was approved and lodged in the Departmental Library in June 1955. By the end of January this year we considered that we had enough data of sufficient interest to warrant publication in this *Journal* and in the trade press.

L. PETERS

C. B. STEVENS

THE UNIVERSITY
LEEDS 2

16th April 1956

¹ Stevens, C. B., and Peters, L., *J.S.D.C.*, **72**, 100 (March 1956).

² Alexander, P., and Stacey, K. A., *Proc. Roy. Soc.*, **A 212**, 274 (1952); Stacey, K. A., *Ph.D. Thesis* (University of London 1952).

³ Martin, J. T., and Standing, H. A., *J. Textile Inst.*, **40**, T 671 (1949).

⁴ Stevens, C. B., and Peters, L., *Dyer*, **115**, 327 (2nd March 1956).

⁵ Ciba and Wittwor, *GP* 832,593.

⁶ Ciba, *BP* 669,192.

⁷ *S. Swiss Patens Application* 29,916.

Notes

Meetings of Council and Committees

April

Council—4th
 Publications—17th
Colour Index Editorial Panel—16th
 Examinations Board—12th
 Perkin Meeting—18th
 Honorary Secretaries and Chairmen of Sections—27th
 Historical Records—27th

Deaths

We regret to report the loss by death of Mr. J. A. Felce (Honorary Secretary of the Leeds Junior Branch 1954-1955), Mr. T. R. Harding, and Mr. R. Richardson.

International Federation of Associations of Textile Chemists and Colourists

The Society has recently joined the above Federation, whose headquarters are in Switzerland. During the 1930s the Society was affiliated to the Federation, but the activities of the latter lapsed on the outbreak of war in 1939. The Swedish society, Svenska Färgeritstekniskförbundet, also has joined the Federation.

The existing members are—

France: Association des Chimistes de l'Industrie Textile (A.C.I.T.)
 Italy: Associazione Italiana di Chimica Tessile e Coloristica (A.I.C.T.C.)
 Holland: Nederlandsche Vereeniging voor Textiel-Chemie (N.V.T.C.)
 Switzerland: Schweizerischer Verein der Chemiker-Coloristen (S.V.C.C.)
 Austria: Verein Oesterreichischer Textilchemiker und Coloristen (V.Oe.C.)
 Germany: Verein der Textilchemiker und Coloristen (V.T.C.C.)

At a meeting of the Council of Delegates held on 10th February 1956, Dr. L. Sessa, of Milan, was elected President of the Federation for the period 1956-1958, in succession to Dr. H. Ris, of Basle. Two joint secretaries—Dr. Crisapuli, of Milan, and Herr M. Peter, of Basle—were elected to succeed the late Dr. E. A. Krähenbühl, of Basle. Herr P. Deck (Merkurstrasse 34, Zürich 7, Switzerland) remains Treasurer of the Federation.

Sundour Jubilee Dinner

A dinner was held in Carlisle on 15th March 1956 to celebrate the fiftieth anniversary of Sundour fabrics (see p. 246), at which the Society was represented by the President, the Honorary Secretary, and the General Secretary.

Election of Fellows

At the meeting of Council held on 2nd May 1956 the following were elected Fellows of the Society—

Marcus Gewing
 (Belfast; Director, Radiant Fabrics Ltd.)
 Douglas Haigh
 (Manchester; Technologist, British Hat and Allied Feltmakers Research Association)
 Stanley John Hill
 (Belfast; Manager, United Chrometanners Ltd., Shrigley Mills)
 John Willie Hirst
 (Melbourne, Australia; Dyehouse Manager, retired)
 Albert Howarth
 (Rostrevor, Northern Ireland; Technical Director, Valley Dyeworks Ltd.)
 Albert Mellor
 (Derby; Chief Colourist, British Celanese Ltd.)
 Reginald Woods
 (West Drayton, Middlesex; Director, Yiewsley Carpet Co. Ltd.)

Celon 6-Nylon

A new polyamide fibre of the 6-nylon (Perlon) type is Celon (BrC). Among properties claimed for Celon are high tensile strength, great resistance to abrasion, and good dyeing properties with a wide range of dyes. It can be heat-set, is resistant to chemicals and dry-cleaning solvents, and can be mixed with wool and viscose rayon staple fibres. Celon is available in tow, top, and staple forms.

Forlion—A New Polyamide Fibre

The firm of Orsi Mangelli, of Forli in Italy, has recently undertaken the manufacture of a new polyamide fibre, formed by polymerisation from goat's milk by the process of Schlak and Kleins. Apart from its strength and light weight, it may be readily milled and is stable to acids. It may be used for clothing, underclothing, parachutes, tent fabrics, etc., and may be blended with cotton, wool, or rayon.

Verel—A Modified Acrylic Fibre

Verel is a modified acrylic fibre produced by Eastman Chemical Products and available only as staple fibre. It has a regain of 3.5-4.0% and a maximum ironing temperature of 300°F., and can be obtained in heat-stabilised or unstabilised states. It is readily dyed with neutral-dyeing acid dyes including the metal-complex types, disperse dyes, and some basic dyes. C.O.C.

Cinematograph Films

A list of textile films was published in the November 1947 issue of the *Journal* (63, 345-350). The following list, compiled by Dr. R. L. Elliott, includes films and a few film strips of possible interest to readers of this *Journal*. The films are classified according to subject in the same manner as the abstracts. A key to the abbreviations follows the list.

Title	Colour*	Sound†	Size (min.)	Time (min.)	Distributors	Notes
MACHINERY						
Air-layer Dryer	—	—	16	6	JD	—
Automatic Clip Jigging Stenter	—	—	16	8	JD	—
Pin Stenters	—	—	16	8	JD	—
Textile-finishing Machinery	—	—	16	45	MP	—
Cashmere Story	C	+	16	16	Pr	Factory scenes at Hawick factory of Pringles'
CHEMICALS						
Pattern for Chemicals	—	+	16 or 35	10	Shell	Chemicals from refinery gases, illustrated by molecular models
Story of D.D.T.	—	+	16	~30	Gy	—
COLOURING MATTERS						
Cibalan Dyes	C	+	16	~30	CDC	—
Discovery of a New Pigment	C	+	16	39	ICI	Monastral Blue
Works by the River	—	+	16 or 35	~33	BASF	Chemical works at Ludwigshafen
PAINTS						
The Hall Mark	C	+	16	15	Halls'	The manufacture of high-grade paint
Paint versus the Sea	—	+	16	11	ICI	Testing of anti-corrosion and anti-fouling paints at Brixham
FIBRES AND FABRICS						
Nobel began it	—	+	16	24	ICI	Development of explosives factory, leading to production of Ardil
Accent on Carpet	C	+	16	20	CT	All carpet-manufacturing processes from fleece to finished carpet
Border Weave	C	+	16	16	IWS	Grading, spinning, scouring, weaving, and dyeing of Border woollen cloth
Fibre to Fabric	—	—	16	75	GI	All processes from shearing the sheep to wearing the garment
Fabrics of the Future	—	+	16	20	GB	—
Dancing Fleece	C	+	16	20	CFL	Cloth, ballet, music-making, and designing of clothes
Flocks of the Veld	—	+	16	22	CFL	South African wool from sheep to user, including dyeing
Light and Airy	C	+	16	20	WATEC	Manufacture of blankets
Pierre que l'on tisse	?	+	16	20	Fr	How asbestos is spun and woven into rope and cloth (French commentary)
Silk	—	+	16 or 35	22	BWA	Sericulture, throwing raw silk, dyeing, weaving, printing, research and testing
Terylene in Industry	—	+	16	~8	ICI	—
Terylene on Parade	—	+	16 or 35	~8	ICI	—
This is Britain—Man of Fashion	—	+	16	10	CFL	Tailoring
DETERGENCY						
New Detergents	—	+	16 or 35	11½	PFB	How detergents work
COLORATION						
Colour	C	+	16	16	ICI	Nature of colour, dyeing and printing, painting, Perkin's Mauve, modern dyemaking

* C Colour film — Black and white

† + Sound film — Silent film

Title	Colour*	Sound†	Size (mm.)	Time (min.)	Distributors	Notes
FINISHING						
Insects astray	—	+	16	~30	Gy	Mothproofing
Shrinkage Control for Tubular Knits	?	?	16	10	CFL	Method for controlling relaxation shrinkage
Wovase Story	?	—	16	30	BMK	All stages of carpet manufacture, including dyeing and moth-proofing
PAPER						
The Gift of Ts'ai Lun	—	+	16	18	USA	Manufacture of paper
ANALYSIS						
Automatic Laboratories	—	+	16	10	BTL	Shown on B.B.C. television
Technique of Sampling	—	+	16	30	ICI	Sampling methods for nitro, coal, cotton fabric (for leathercloth), and ammonia; testing a confined atmosphere for dangerous fumes
MISCELLANEOUS						
Atomisation	—	+	16 or 35	17	Shell	Principles and mechanism of the atomisation of liquids
Nagana	C	+	16	~30	Gy	Produced by South African Government
Full-time job	—	+	16	20	ICI	Dialogue film showing medical and dental facilities in large chemical works, and the treatment of an industrial accident
Treatment for Shock	—	+	16	6	ICI	First-aid treatment
Man against Insect	—	+	16	21	ICI	Man's fight against insects and the story of Gammoxane
The Rival World	+	+	16 or 35	25	Shell	Man's struggle against insects and organised scientific control in critical areas
The Story of Antrycide	—	+	16	27	ICI	Research on drug for "tsetse fly disease", including many scenes of wild game in Africa
Get off the Hose	—	+	16	16	ICI	Interference of controls and paperwork with international commerce
Feature Story	—	+	16	50	ICI	Early history of chemical industry in Britain; history, organisation, and research results of ICI
Enterprise	C	+	16	22	ICI	Cartoon dedicated to the spirit of enterprise in industry; structure of ICI and how its income is spent
Balance 1950	C	+	16	9	ICI	Cartoon explaining ICI's balance sheet
Film Strips (with lecture notes)						
Surface Coatings	—	—	35	—	Shell	Raw materials, application, paints, lacquers
Cloth Construction	+	—	?	—	IWS	Weave structure, design, and special finishes
Scientific Story of Wool	?	—	?	—	IWS	Biology, chemistry, and physics
Detergents and Wool	—	—	35	—	Shell	Manufacture of wool goods, from raw wool to yarn, and from yarn to fabric
Light into Colour	C	—	35	—	Unicorn	Composition of spectrum and use of colour filters
Rayon Industry—Historical	—	—	35	—	CG	} Manufacture of viscose rayon from raw material to finished fabric
Rayon Industry—Contemporary	—	—	35	—	CG	
Silk from Mulberry	—	—	35	—	BIF	Production of silk from silkworm to fabric
Fibre from Flax	—	—	35	—	BIF	} Preparation of flax fibre and linen fabric
Linen—Flax Field to Linen Fabric	—	—	35	—	VIS	
* C Colour film	— Black and white				† + Sound film	— Silent film

Names and Addresses of Distributors

BASF	Badische Anilin- und Soda-Fabrik AG, Ludwigshafen a. Rhein, Germany
BIF	British Instructional Films Ltd., Mill Green Road, Mitcham, Surrey
BMK	Blackwood Morton & Sons Ltd., 99 Glassford Street, Glasgow C.1
BTL	Public Relations Officer, Baird & Tatlock (London) Ltd., 14-17 St. Cross Street, London E.C.1
BWA	Brocklehurst-Whiston Amalgamated Ltd., Hurdsfield Mills, Macclesfield
CDC	The Clayton Dyestuffs Co. Ltd., Clayton, Manchester 11
CFL	Central Film Library, Government Buildings, Bromyard Avenue, London W.3
CG	Common Ground Ltd., Sydney Place, London S.W.7
CT	Carpet Trades Ltd., Kidderminster
Fr	Institut Français du Royaume-Uni*, Queensberry Place, London S.W.7
GB	Gaumont-British Distributors Ltd., Film House, Wardour Street, London W.1.
GI	George Ingham & Co. Ltd., Greetland, Halifax, Yorkshire
Gy	The Geigy Co. Ltd., Rhodes, Middleton, Manchester
Halls	John Hall & Sons (Bristol & London) Ltd., Petherton Road, Bristol 4
ICI	ICI Film Library, Imperial Chemical House, Millbank, London S.W.1
IWS	International Wool Secretariat, Dorland House, 18-20 Regent Street, London S.W.1
JD	John Dalglish & Sons Ltd., Industrial Estate, Thornliebank, Glasgow
MP	Mather & Platt Ltd., Platt Works, Manchester 10
PFB	Petroleum Film Bureau, 29 New Bond Street, London W.1
Pr	Pringles of Scotland Ltd., 12a Savile Row, London W.1
Shell	Publicity Department, Shell Chemical Co. Ltd., Norman House, 105-109 Strand, London W.C.2
Unicorn	Unicorn Head Visual Aids Ltd., Broadway Chambers, 40 Broadway, London S.W.1
USA	United States Information Service, 1 Grosvenor Square, London W.1
VIS	Visual Information Service, 168a Battersea Bridge Road, London S.W.11
WATEC	Wool & Allied Textile Employers' Council, Lloyds' Bank Chambers, Bradford 1, Yorkshire

* A French organisation having a large number of technical films is La Cégos, 33 rue Jean Goujon, Paris, but it is not certain whether these would be available to borrowers in Great Britain.

OBITUARY NOTICES

Louis Diserens

Monsieur Louis Diserens died on 7th January 1956 at his home at Thann (Haut Rhin), France. His age was 65 years.

He was born in Moscow in 1891, and ten years later his parents went to live in Lausanne. After attending school, he studied at the Federal Polytechnic in Zürich and obtained his degree of Ingénieur-Chimiste. After further studies at the University of Lausanne, he became a doctor of science.

From 1915 until 1920 Diserens worked as textile colourist at the factory of Messrs. Morosov in Tver (Russia) and later at the textile-printing firm of E. Zundel in Moscow. In 1915 he married the sister of Marcel Bader, the inventor of the Indigosols.

Diserens and his family had to leave Russia after the revolution, and he became a colourist at Messrs. Scheurer Lauth & Cie., Thann, and was later appointed director and general manager. He was connected with this firm for 36 years, until his death.

Diserens devoted much of his spare time to literary and research work, and he wrote, during 1947-1951, four volumes of *Neueste Fortschritte und Verfahren in der chemischen Technologie der Textilfasern* (Verlag Birkhäuser, Basle) and, during 1950-1953, two volumes of *Neue Verfahren in der Technik der chemischen Veredlung der Textilfasern*, the third volume of which was recently announced

for early publication. His books were first published in French, then translated into German, and an English edition of the first two volumes of the first series was published under the title *The Chemical Technology of Dyeing and Printing* (New York: Reinhold Publishing Corp., 1948 and 1949).

Diserens's books can best be described as an encyclopaedia on textile bleaching, dyeing, printing, and finishing, and never before has such a comprehensive work been undertaken and published. It was, and still is, unique in presentation and content, and, apart from very thorough and assiduous study of literature and patents, the author was able to write, and to teach, from his long and wide practical experience. Since the first publication, further revised and enlarged editions have been printed. Diserens's books were very well received. They have been reviewed in this *Journal*.

His name as the author of the series of books will live on and will long be remembered.

He became a member of the Society in 1949.

A. F. KERTESS

David Gillespie Marshall

Mr. D. G. Marshall, joint managing director of The Yorkshire Dyeware & Chemical Co. Ltd., died on 8th February 1956 in the Brotherton Wing of the Leeds General Infirmary after an illness lasting about one month. He was 47 years of age.

David Marshall was born at Motherwell, and on leaving college commenced his business life on the staff of the Glasgow office of I. G. Dyestuffs Ltd. In 1940 he joined Y.D.C., where he was engaged on the export and commercial side of the business, his duties in the export field taking him to practically every European country and to North America.

He served on many committees, was at one time a member of the Leeds Chamber of Commerce, and had been for many years associated with the Dyestuffs Group of the Association of British Chemical Manufacturers. He was the leader of the Board of Trade Dyestuffs Mission to Germany in 1948.

Although his many business duties prevented Mr. Marshall from personally taking an active part in the work of the Society, he gave every encouragement to others to do so.

In every field of activity he displayed whole-hearted enthusiasm. During the war he held a Commission in the 9th Battalion, West Riding Home Guard.

"D.G." was a man of ideas, and was always anxious to encourage the younger generation. His death is a great loss to his many friends, his co-directors, and the staff of Y.D.C.

He leaves a widow, a son, and two daughters.
A. THOMSON

New Books and Publications

Review of Textile Progress

Volume VI, 1954

Published jointly by the Textile Institute and the Society of Dyers and Colourists. Pp. 586. Price, 37s. 6d. (30s. 0d. to members of the Institute or the Society).

The *Review of Textile Progress* is now so familiar that we tend to take it for granted, forgetting that its publication largely depends on voluntary work.

The high standard achieved by the panel of editors over a period of years is fully maintained in the current volume, which shows, as usual, some variation in content compared with the previous volume. The section on Felts is omitted, but there are new sections on Bleaching of Cellulosic Fibres (pp. 16), Narrow Fabrics (pp. 20), and Synthetic Fibres in Cordage (pp. 3). Two overseas contributors, Mr. S. B. McFarlane and Professor K. Venkataraman, have written the sections on Synthetic Fibres and on Colouring Matters. This innovation is highly successful, Mr. McFarlane's article being especially interesting. There are eleven new authors and, in the words of the Chairman of the Joint Committee, "we have to say farewell to many good friends upon whose work the fine reputation of the *Review* is founded".

As in previous years, the sections on dyeing, printing, and finishing occupy a considerable portion of the volume, and they are essential reading for all members of the Society concerned with the latest developments in these branches of our industry.

C. L. BIRD

Fifty Years of Sundour

Morton Sundour Fabrics Ltd. [Carlisle 1956.] Pp. iv + 40. No price.

This interesting booklet consists mainly of a reprint of a lecture given by the late Sir James Morton to the Royal Society of Arts in February 1929. A long summary of this lecture appeared in this *Journal* at the time (J.S.D.C., 45, 148 (1929)), but the subject is of so much interest that a brief outline will not, perhaps, be out of place.

In 1902 James Morton had difficulty, owing to fading, in recognising some of his own fabrics which had been on display in Liberty's windows in Regent Street for only one week. This led him to expose patterns at Penrith and in India, and, as a result, a small range of colours was produced carrying a guarantee of replacement if found to fade or not to withstand an ordinary laundry wash.

The range of dyes originally included Alizarin and mineral pigments, but the anthraquinoid vat dyes became available just in time to enable him to complete his range of hues, although their practical application presented many problems. The resistance of these dyes to fading led to the success of the guaranteed fastness plan and to the coining of the word "Sundour" as its trademark.

A further stage in the application of fast colours was reached when, in 1909, it was decided to depart from the previously accepted practice of dyeing in yarn form and to attempt piece dyeing with vat dyes. This new development demanded a new technique, which was worked out first in the laboratory and was then successfully transferred to the works.

The outbreak of war in 1914 cut off the supply of vat dyes from Germany and, rather than lower the standard of fastness, James Morton decided to make indanthrone and flavanthrone from 2-aminoanthraquinone, which was itself made from "silver salt" (anthraquinone-2-sulphonic acid). The story of their many failures and eventual success as early as March 1915, when 20 lb. of this type of vat dye was produced in this country for the first time, makes most interesting reading. This success must have given James Morton great satisfaction as well as enabling him to prove to one dye manufacturer that "weavers could make dyes".

By October of that year a satisfactory 8-cwt. autoclave had been obtained, but it was becoming apparent that it would be necessary to make "silver salt" themselves. This entailed not only the preparation under war conditions of anthracene of at least 95% purity from the commercial

product, which contained only 40%, but also its sulphonation—a task which most would have considered impossible in the circumstances.

By summer of 1916 Solway Blue (Alizarine Sapphirole) was being manufactured, by the end of the war 50% of the annual pre-war import of this dye was being made, and by 1919 the production amounted to 150% of such imports. During 1919 an 80-acre site at Grangemouth was purchased, and the name of the firm was changed from Solway Dyes Co. to Scottish Dyes Ltd.

At that time Mr. Morton was in America bargaining for the British rights of the process for the production of phthalic anhydride from naphthalene by air oxidation. Both these moves were to have far-reaching results.

When the Government imported German dyes to the value of £7,000,000 by way of reparation, the result was a heavy blow to the new British Dyestuff Industry. The slump, however, gave the chemists of Scottish Dyes Ltd. an opportunity of

carrying out research instead of spending their time solely on works control, and the result was the introduction of Caledon Blue RC, of the first green vat dye (Caledon Jade Green) in 1922, and of Soledon Jade Green, the first anthraquinone vat dye to be put on the market in a soluble form.

The story of this remarkable achievement does not end here, for progress has been maintained in the production of dyes (10 tons of vat dye were produced each week by 1928), in improved dyeing processes such as the molten-metal process associated with the name of Standfast Dyers & Printers Ltd., a subsidiary of Morton Sundour, and in development of improved and speedier knitting machinery.

All this is in the true tradition of Perkin, who not only discovered Mauveine but found how to apply it, and it is very fitting that the Golden Jubilee of Morton Sundour should coincide with the Perkin Centenary Celebrations of 1956.

A. THOMSON

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., 68, 23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index

I—PLANT; MACHINERY; BUILDINGS

Drying by Infrared Radiation generated by Electrically Conducting Glass

E. Plumat and E. Deliere

Ind. chim. belg., 20, 961-971 (1955);
Chem. Abs., 50, 617 (25 Jan. 1956)

Glass is an ideal radiator for long-wave infrared radiation and gives a high yield with very low convection losses. The spectral composition of the emitted radiation must be adapted to the spectral absorption of the material being heated. Application of radiation panels for drying textiles and paints is discussed. C.O.C.

PATENTS

Automatic Control of Wool Oiling

Pneumatic Conveyors (Huddersfield)

BP 745,080

When wool is oiled by passing through a suction wool duct, mechanical control of oiling may be effected by means of a rod hanging in the duct so that it is displaced from the vertical by passage of wool but not by air flow alone. The lever is connected to a cam, lever, link, and dashpot system whereby deflection automatically causes the oil to flow, and return to vertical causes it to stop. The actual oil control may be through a mercury switch mounted on the lever for operating the oil valve. Mention is also made of an entirely different system comprising a photoelectric cell energised by a light-beam passing across the duct. J.W.B.

Thread-advancing Thread-drying Reel

Courtaulds

BP 745,885

Wet Spinning of Viscose Rayon

Courtaulds

BP 744,704

Apparatus is described for washing freshly spun viscose rayon threads with a succession of liquids under the minimum tension. W.G.C.

Maintaining Uniform and Constant Temperature of the Dye Liquor in Winch Dyeing and Similar Machines

Rodney Hunt Machine Co.

USP 2,706,391

The vat has a false perforated bottom. Between the false and true bottoms there are heating coils. A pump withdraws liquor from the upper part of the bath and

returns it to a spot between the two bottoms at a point below where the fabric is moving most slowly. C.O.C.

Controlling the Speed of Rollers feeding Fabric into a Machine

Samco Holding Corpn.

BP 742,431

Control apparatus for the speed of feed rollers to ensure that the fabric remains constantly relaxed irrespective of any shrinkage in length. C.O.C.

Reel-type Drier for Fabric

Samco Holding Corpn.

BP 742,429

In a reel-type drier, e.g. of the type described in BP 540,054 (*J.S.D.C.*, 58, 43 (1942)), the fabric is permitted to shrink to the maximum extent, without any internal stresses being introduced into it while it is in the drier, by controlling the speed of each successive reel by the accumulation of completely relaxed portions of the fabric. C.O.C.

Pelleting Carbon Black

Godfrey L. Cabot

BP 745,933-4

Continuous Process for rendering Fabric Dimensionally Stable (X p. 257)

II—WATER AND EFFLUENTS

Biochemical Behaviour of Synthetic Detergents

C. N. Sawyer, R. H. Bogan, and J. R. Simpson

Ind. Eng. Chem., 48, 236-240 (Feb. 1956)

The susceptibility of various synthetic detergents to biological oxidation was measured, in the presence of sewage, by the biological oxygen demand test, and by the determination of oxygen utilisation. The results were confirmed by measuring the persistence of detergents, alone and in the presence of sewage, in river water. The detergents varied greatly in susceptibility to attack, depending on structure and molecular size. Alkyl sulphates, sulphonated amides and esters, and *n*-dodecylbenzenesulphonate were degraded fairly easily, and disappeared rapidly in river water; but *k*erylbenzenesulphonate and tetrapropylenebenzenesulphonate were quite resistant, and had half-lives of 7 and 16 days respectively, in river water. Non-ionic detergents also showed considerable

variation, those with large molecules being relatively resistant. The biologically resistant detergents are liable to be troublesome in sewage treatment. W.K.R.

Detergents in Water Supplies

J. C. Vaughn and R. F. Falkenthal

Ind. Eng. Chem., 48, 241-245 (Feb. 1956)

Problems due to the presence of detergents in water supplies are discussed. As many detergents pass through sewage treatments relatively unchanged, water supplies which are subject to re-use can build up an appreciable detergent content. Methods of treatment for removing an anionic detergent (20 p.p.m.) from water were evaluated. The most effective was treatment with settled sediment taken from filtration-plant settling basins. Sediments from water coagulated with aluminium sulphate and with chlorinated ferrous sulphate were equally effective. The detergent is removed by adsorption. Among other treatments, activated carbon and chlorine dioxide were effective, but very high dosages were required. Pretreatment with a cationic material, rosin-amine acetate, permitted complete removal of detergent by alum-silicate coagulation, but this treatment could not be used in bulk because the amine is a skin irritant. W.K.R.

Conditions in Activated Sludge Process during Frothing

G. P. Edwards and M. E. Ginn

Ind. Eng. Chem., 48, 246-250 (Feb. 1956)

The presence of detergents in sewage may cause frothing in the activated sludge treatment. From experiments with artificial sewages it is shown that, during the aeration cycle in activated sludge treatment, much of the detergent is rapidly adsorbed by the sludge. Frothing appeared to be independent of surface tension and oxidation potential of the liquor, which both increased slowly during aeration. No explanation was found for the development of froth after some hours' aeration. W.K.R.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

New Hydrate of Sodium Perborate

D. W. van Gelder

Rec. Trav. chim., 75, 117-126 (Feb. 1956)

A new hydrate of sodium perborate, $\text{NaBO}_3 \cdot 3\text{H}_2\text{O}$, is reported. It may be prepared by stirring equal weights of the tetrahydrate (the normal commercial salt) and water for 4 hr. at 50°C., then filtering, and drying under vacuum at 40°C.; or by keeping solutions of the tetrahydrate (in the absence of catalytic metals) for long periods at 25-50°C. Above 15°C. the tetrahydrate is metastable in solution. The trihydrate is more stable to heat and storage, and, unlike the tetrahydrate, it can be kept at slightly elevated temperatures (up to 50°C.) without caking. W.K.R.

Structure of Dithionite

J. D. Dunitz

J. Amer. Chem. Soc., 78, 878-879 (20 Feb. 1956)

X-Ray analysis of crystals of anhydrous sodium dithionite (hydrosulphite) indicates that the dithionite anion is a pair of SO_2^- units linked by a weak S-S bond. Thus the reducing action of dithionite proceeds simply by loss of an electron to any suitable acceptor with formation of SO_2 . C.O.C.

PATENTS

Salts of Polyesters of Aliphatic Sulphodicarboxylic Acids—Auxiliary Agents

American Cyanamid Co.

BP 745,412

The products obtained by condensing 2 mol. of a fatty acid mono- or di-glyceride (acid of > 7°C) with 1 mol. of the ester obtained from 1 mol. of an alkylene or polyoxy-alkylene glycol and 2 mol. of an ethylenically unsaturated aliphatic dicarboxylic acid or anhydride (unsaturated group is α to a carbonyl group) can be used as softening agents having antistatic properties. When used in antistatic compositions containing inorganic salts they inhibit crystallisation of the salts. C.O.C.

Soap Composition resistant to Hard Water

Unilever

BP 745,367

A mixture of soap, a non-ionic detergent, and a compound of formula $\text{R}^1\text{R}^2\text{N}[\text{CH}_2]_x\text{COOM}$ ($\text{R}^1 = \text{Alk}$ of 12-

20C; $\text{R}^2 = \text{H}$ or Alk ; $\text{M} = \text{Na}$ or K ; $x = 1$ or 2), e.g. the Na salt of an N-mono-alkyl- β -alanine, does not form a precipitate of insoluble soaps when used in hard water under a wide variety of conditions. C.O.C.

Wool Lubricant for improving Milling

E. F. Drew & Co.

BP 745,175

An acid-stable wool lubricant designed to give an attractive handle after acid milling comprises an emulsion of a polyethylene glycol 325-850 monoester of a higher fatty acid, an unsaturated glyceryl triester of a higher fatty acid, and a condensation product of an ethanalamine with the fatty acids of a vegetable or animal oil. In one example the lubricant comprises polyethylene glycol 400 mono-oleate (15 parts by wt.), diethanolamine coconut-oil fatty acid condensation product (7.5), peanut oil (7.5), pale paraffin oil (70), and oleic acid (0.5-1). This blend (10-50%) is emulsified with water and applied to wool fabric (1-10% on wt. of fibre). After carbonising, a solution is prepared of 2-8 oz. of polyethylene glycol 350 monolaurate ethyl ether per gal., and applied to the fabric so that 50-125% by wt. is taken up, and the fabric is milled. Strength is improved and subsequent dye adsorption is more even. J.W.B.

Wool Lubricant readily removed by Scouring

Esso Research & Engineering Co.

USP 2,706,713

A mineral lubricating oil and an oil-soluble petroleum sulphate are mixed with 0.5-5.0% of their weight of the non-ionic detergent obtained by condensing ethylene oxide with a C_{13} - C_{21} unsaturated fatty acid. C.O.C.

N-Hydroxymethylpolypyrrolidones—Finishing Agents

Arnold Hoffman

BP 743,742

Polypyrrolidones are converted into water-soluble N-hydroxymethyl products by treating with formaldehyde in presence of a monohydroxycarboxylic acid, e.g. glycolic acid. The products are used as coating or impregnating materials for textiles, a finish fast to washing being obtained by baking the treated material. W.G.C.

Rotproofing Agents

Chemische Industrie "Rids"

BP 745,168

Compounds of formula—



($\text{R}^1 =$ aromatic radical, linked directly to the N, in which at least one H has been replaced by a polar group, preferably one having a double or triple bond; $\text{Z} = \text{R}^2\text{R}^3$ or CR^2R^3 ; R^2 and $\text{R}^3 = \text{H}$ or subst. or unsubst. aliphatic or aromatic groups) are much stronger fungicides than similar compounds in which $\text{R}^1 = \text{H}$, aliphatic, or unsubst. aromatic radical. C.O.C.

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Explosion of Zinc Benzenediazonium Chloride

G. D. Muir

Chem. and Ind., 58-59 (14 Jan. 1956)

Report of an explosion of zinc benzenediazonium chloride after prolonged drying over P_2O_5 in a vacuum oven. A.J.

Hammett's σ -values for $-\text{NH}_2$ and $-\text{NH}_3^+$

A. V. Willi and W. Meier

Helv. Chim. Acta, 39, 318-322 (Feb. 1956).

Acidity Constants of Benzenesulphonamides

A. V. Willi

Helv. Chim. Acta, 39, 46-53 (Feb. 1956)

Homologues of 2:3-Dihydroxynaphthalene

Ng. Ph. Buu-Hoi and D. Lavit

J. Org. Chem., 21, 21-23 (Jan. 1956)

The 1-methyl, 6-ethyl, and 6-n-propyl deriv. of 2:3-dihydroxynaphthalene are synthesised from 2:3-dimethoxynaphthalene, together with other, related cpd. H.E.N.

Dyes as Photographic Sensitisers

H. Wolff

Fortschr. Chem. Forsch., 3, 503-602 (1955):

Chem. Abs., 50, 709 (25 Jan. 1956)

Review, 144 references.

C.O.C.

Benzimidazoles. IV—Azo Colouring Matters

F. Montanari

Gazz. chim. ital., **85**, 981-988 (1955);
Chem. Abs., **50**, 1317 (25 Jan. 1956)

Affinities for cellulose acetate and nylon are given for a number of azo derivatives of benzimidazole, e.g. 4-(dimethylaminophenylazo)-benzimidazole, 4-(diethylaminophenylazo)-benzimidazole, 2-[p-(dimethylamino-phenylazo)phenyl]-benzimidazole, and 2-[p-(dimethylaminophenylazo)phenyl]-benzimidazole, together with the fastness of the dyeings to washing and perspiration.

C.O.C.

Pyrrrole Dyes. IV—The Ehrlich Reaction of Pyrroles and Indoles

A. Treibs and E. Herrmann

Hoppe-Seyler's Z. physiol. Chem., **299**, 168-185 (1955);
Chem. Abs., **50**, 943 (25 Jan. 1956)

The equilibrium position between a pyrrole, p-(CH₃)₂N-C₆H₄-CHO (I), a pyrrolyl-(dimethylaminophenyl)-methene salt (Ehrlich dye) (II), and a (dimethylaminophenyl)dipyrrolylmethane (III) depends on the substituents of the pyrrole ring. Formation of II is favoured by alkyl groups and excess of I, and of III by negative substituents and excess of pyrrole. Acids split III to C₆H₅N(CH₃)₂ and a dipyrrolylmethene salt. C.O.C.

Production and Properties of 3-Amino-10-p-anilino-phenylphenazonium Chloride

O. N. Nikiforova

Trudj Khim.-Met. Inst. Zapad-Sibir. Filiala Akad. Nauk S.S.S.R., (7), 63-74 (1953);
Referat. Zhur. Khim., 44049 (1954);
Chem. Abs., **50**, 575 (10 Jan. 1956)

When wool is dyed black with 4-nitrosodiphenylamine hydrochloride a violet dye is produced in the dye vat, and hitherto it has been assumed that it was an intermediate in the formation of the black dye. Wool (7 g.) was boiled with 4-nitrosodiphenylamine hydrochloride (20 g.) in distilled water (4 litres) for 70 min., the liquor filtered, and the dye salted out with NaCl. This gave 3-amino-10-p-anilino-phenylphenazonium chloride (I), which was purified by reprecipitation, extracted with ether, and finally recrystallised from butanol, when black-violet crystals were obtained. Treating this compound with aq. Na₂CO₃ and extracting with ether yielded 3-imino-10-p-anilino-phenylphenazine (II). Both I and II dyed wool, silk, and tannin-mordanted cotton a clear violet, which did not darken under any treatment. Thus I cannot be an intermediate in the formation of the black dye. It is a photographic desensitiser. II (8 g.) boiled in acetic anhydride (55 ml.) for 4 hr. yielded the diacetyl derivative, which dyed wool, silk, and tanned cotton brown and which is a weak photographic sensitiser.

C.O.C.

Cyanine Dyes containing a Tertiary Butyl Group

I. N. Zhmurova and Z. M. Ivanova

Ukrain. khim. zhur., **21**, 504-509 (1955);
Chem. Abs., **50**, 707 (10 Jan. 1956)

Introducing *tert*-butyl groups into the 5:5' and 6:6' positions of the benzothiazole ring of thiocarbocyanines only slightly affected the maximum absorptions of the dyes, in this resembling the effect of introducing CH₃ groups into the same positions. C.O.C.

Pyrylium Salts

R. Wizinger, A. Grüne, and E. Jacobi

Helv. Chim. Acta, **39**, 1-4 (Feb. 1956)

4:6-Diphenyl- α - and 2:6-diphenyl- γ -pyrone are condensed with tertiary aromatic amines or diarylethenes to yield coloured salts. H.E.N.

Preparation of Triarylpyrylium Salts

R. Wizinger, S. Löisinger, and P. Ulrich

Helv. Chim. Acta, **39**, 5-15 (Feb. 1956)

This consists in condensing either 1 mol. of a benzaldehyde with 2 mol. of an acetophenone or 1 mol. of an acetophenone with 1 mol. of a chalcone. The colour of the products is discussed in relation to their constitution and also that of the corresponding pyridinium salts. H.E.N.

Thiopyrylium Salts

R. Wizinger and P. Ulrich

Helv. Chim. Acta, **39**, 207-216 (Feb. 1956)

2:4:6-Triarylthiopyrylium salts are readily obtained from the corresponding pyrylium opd. by reaction with

sodium sulphide in aqueous acetone. They are even more deeply coloured. H.E.N.

Thiopyrylocyanines

R. Wizinger and P. Ulrich

Helv. Chim. Acta, **39**, 217-222 (Feb. 1956)

4-Methyl-2:6-diphenyl- and 2-methyl-4:6-diphenyl-thiopyrylium perchlorates are synthesised and used to prepare symmetrical and unsymmetrical cyanines. H.E.N.

Syntheses of Heterocyclic Compounds of Nitrogen. XCV—Photosensitising Dyes. 14

T. Takahashi and K. Satake

J. Pharm. Soc. Japan, **75**, 14-20 (1955);
Chem. Abs., **50**, 1003 (25 Jan. 1956)

A very large number of syntheses of the following type are given. 2:6-CH₃((CH₃)₂N)C₆H₃N-CH₃I (0.33 g.), p-(C₆H₅)₂NC₆H₄CHO (0.18 g.), C₆H₅OH (5 ml.), and piperidine (2 drops) are heated for 60 min. to yield, on recrystallisation from CH₃OH, 0.3 g. of the bright green 2:6-(p-(C₆H₅)₂N-C₆H₄-CH:CH)((CH₃)₂N)-C₆H₃N-CH₃I. C.O.C.

Polynuclear Aromatic Hydrocarbons. I—A New Route to Anthracene and 1:2-Benzanthracene DerivativesO. P. Vig, S. V. Keskar, V. P. Kubba, and S. M. Mukherji
J. Indian Chem. Soc., **32**, 697-701 (Nov. 1955)**Anthraquinone and Anthrone Series. XVII—Synthesis of 1:3:7-Trihydroxyanthraquinone and 1:3:8-Trihydroxyanthraquinone**

N. Parkash and K. Venkataraman

J. Sci. Ind. Research (India), **13B**, 825-828 (1954)**Fluorinated Aminoanthraquinone Dyes**J. B. Dickey, E. B. Towne, M. S. Bloom, G. J. Taylor, D. J. Wallace, J. Sagal, M. A. McCall, and D. G. Hedberg
Ind. Eng. Chem., **48**, 209-213 (Feb. 1956)

A new series of pink to violet acetate-rayon dyes was prepared by reaction of leuco-quinizarin with various fluoroalkylamines, followed by oxidation of the resulting leuco dyes to 1-fluoroalkylamino-4-hydroxyanthraquinones. Some of these dyes had exceptionally good fastness to light and to gas-fume fading. The N-fluoroalkyl groups improved the fastness and altered the hue from violet towards pink in the following order: CH₃-CF₂-CH₂-CH₂-CH₂-CH₂-CH₂-CF₃ < CH₃-CF₂-CH₂-CH₂-CF₃ < CH₃-CF₂-CH₂-CF₃ < CH₃-CF₂-CH₂-CF₃-CH(CH₃)₂. The 1:4-bis-(fluoroalkylamino)anthraquinone dyes are bluer, but poorer in fastness and dyeing properties, than the corresponding 1-fluoroalkylamino-4-hydroxyanthraquinones. The preparation of a number of new fluoroalkylamines is described. In another series of dyes, the CF₃ group was introduced into the 2 position in the aminoanthraquinone nucleus by reaction of 1-amino-4-bromo-2-trifluoromethylanthraquinone with various o- and p-hydroxy polyethoxyanilines. These gave bright blues on acetate rayon, of excellent fastness to light and good fastness to gas-fume fading, and in general were superior to corresponding dyes with a CN, CO-NH₂, SO₂-CH₃, S-CH₃, or CH₃ group in the 2 position. W.K.R.

Condensation of Phthalideneacetic Acid with Naphthalenes to form Benzopyrenequinones

H. E. Schroeder, F. B. Stilmar, and F. S. Palmer

J. Amer. Chem. Soc., **78**, 446-450 (20 Jan. 1956)

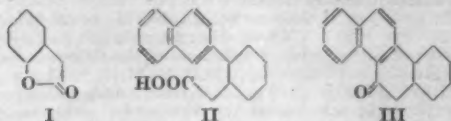
A remarkably simple one-step synthesis of benzopyrenequinones is to condense phthalideneacetic acid with either naphthalene, its homologues, fluoranthene, or anthracene in presence of anhydrous HF at moderate temperatures. In almost every case there result highly coloured substances which can be separated into a bicarbonate- or carbonate-soluble fraction, usually representing elimination of 1 mol. of water from the reactants, and a more deeply coloured fraction, analytically corresponding to elimination of 2 mol. of water. In many cases as much as a 96% yield of the alkali-insoluble material can be obtained. The alkali-insoluble products are of two types depending upon the starting materials employed. Naphthalene, methyl-naphthalenes, anthracene, and fluoranthene yield vat-dyeable substances, probably quinones homologous with the 3:4-benzopyrene-1:5-quinone obtained when naphthalene is used. Chloro-, bromo-, methoxy-, and methyl-thio-naphthalenes, pyrene, perylene, and chrysene yield more deeply coloured, reducible, but not vat-dyeable, substances, whose structure has not yet been determined. C.O.C.

New Synthetic Route to Chrysene Derivatives

D. D. Phillips

Chem. and Ind., 54 (14 Jan. 1956)

trans-2-Hydroxycyclohexane-acetic acid lactone (I) (formed from cyclohexene oxide) undergoes Friedel-Crafts condensation with naphthalene to give 2-β-naphthylcyclohexane-acetic acid (II), which may be cyclised to the ketone III. This is reduced by lithium aluminium hydride to the corresponding alcohol, which is dehydrogenated by heating at 270°C. over a palladium catalyst to yield chrysene. Overall yield from I is ca. 40%.



A.J.

Effect of Pressure on the Semi-conductivity of isoViolanthrone

H. Inokuchi

Bull. Chem. Soc. Japan, 28, 570-572 (Oct. 1955)

The electrical resistivity of a rod of isoviolanthrone is diminished rapidly from 10^{11} to 5×10^9 ohm-cm. when compressed to 80-100 kg./cm.². This is due to plastic deformation of the sample. At greater pressures resistivity decreases slowly and reversibly, owing to elastic deformation of the crystals, to 1.2×10^7 ohm-cm. at 8.4×10^3 kg./cm.². This is thought to be associated with electron overlap between adjacent molecules. Resistivity decreases with increasing temp. The resistivity of violanthrone also decreases with increasing pressure.

A.J.

Indole. I—Structure of "2-Aminoindole"

J. Kebrie and K. Hoffmann

Helv. Chim. Acta, 39, 116-131 (Feb. 1956)**Effect of Copper Cyanide upon the Formation in vitro of Melanin**

S. Isaka and M. Akino

Nature, 177, 184-185 (28 Jan. 1956)

Although CN⁻ normally inhibits Cu oxidases, the addition of KCN to a 3:4-dihydroxyphenylalanine (I)-Cu²⁺-xanthopterin (II) system accelerates the autoxidation of I to melanin to a greater extent than does II-Cu²⁺ alone. Copper cyanide also accelerates the autoxidation. The accelerating effect of Cu²⁺ on the autoxidation of pyrocatechol (III) is checked, but not prevented, by II. Copper cyanide is also effective but is not greatly superior to Cu²⁺ alone; Cu(CN)₂ and II-Cu²⁺ thus appear to function in different ways. The autoxidation of III is slightly accelerated by Cu²⁺ and is inhibited by CN⁻, but it is markedly enhanced by the two together; max. acceleration occurs with a 1:2 ratio of Cu²⁺:CN⁻. The optimal mixing ratio for II-Cu²⁺ is 1:1. Addition of certain chelating agents (including II) to the Cu(CN)₂-III system decreases the rate of oxidation. These facts suggest that certain complexes of Cu²⁺ and CN⁻ are formed, and that they act catalytically; their substrate may be the bidentate donor derived from III and its derivatives. The autoxidation of I is affected in the same way as by CN⁻ by other substances, e.g. CN⁻ > CNS⁻ > NH₂ (in order of activity), but bivalent metal ions other than Cu²⁺ are not effective.

J.W.D.

Synthesis and Bleaching of Rhodopsin

G. Wald and P. K. Brown

Nature, 177, 174-176 (28 Jan. 1956).**Rhodopsin****VIII—N-Retinyldenemethylamine an Indicator Yellow Analogue**

G. A. J. Pitt, F. D. Collins, R. A. Morton, and P. Stor

Biochem. J., 59, 122-128 (1955)

The above has the constitution *N*-[3:7-dimethyl-9-(2:6:6-trimethyl-1-cyclohexen-1-yl)-2:4:6:8-monotetraenylidene]methylamine and contains the same chromophoric group as retinene oxime.

IX—pH and the Hydrolysis of Indicator Yellow

R. A. Morton and G. A. J. Pitt

Ibid., 128-134*Chem. Abs.*, 50, 897 (25 Jan. 1956)Study of the stability of *N*-retinyldenemethylamine

in aqueous soln. at various pH shows that *N*-retinyldenemethylammonium ions are stable, but that unchanged *N*-retinyldenemethylamine ions hydrolyse to retinene. C.O.C.

Synthesis of Carotenoids**I—Technical Synthesis of β-Carotene**

O. Isler, H. Lindlar, M. Montavon, R. Rüegg, and P. Zeller

Helv. Chim. Acta, 39, 240-259 (Feb. 1956)

The process, used industrially in both Switzerland and the U.S.A., starts with β-ionone, which is lengthened to the β-C₁₅-aldehyde as in the vitamin A synthesis (*ibid.*, 30, 1911 (1947)). By acetalisation, condensation with vinyl ether, and treatment with acid, the new β-C₁₅-aldehyde is obtained, which, using propenyl ether similarly, leads to the β-C₁₉-aldehyde (I). Two mol. of I are linked with acetylene either directly by use of acetylenadi-magnesium bromide or in two stages with lithium acetylide in liquid ammonia followed by a Grignard reaction. Water is split off from the resultant β-C₄₀-diol, giving 15:15'-dehydro-β-carotene, the central triple bond of which is partly hydrogenated and the 15:15'-cis-β-carotene isomerised to β-carotene by treatment in petroleum ether at 90-100°C. for 10 hr. All its properties are identical with those of the epd. obtained from natural sources.

II—Synthesis of Intermediates

O. Isler, M. Montavon, R. Rüegg, and P. Zeller

Ibid., 259-273**III—Synthesis of 3:4:3':4'-Bisdehydro- and 3:4-Monodehydro-β-carotene**

O. Isler, H. Lindlar, M. Montavon, R. Rüegg, and P. Zeller

Ibid., 274-282

H.E.N.

Anthochlor Pigments**XI—Constituents of *Coreopsis maritima*. Re-investigation of *Coreopsis gigantea***

T. A. Geissman, J. B. Harborne, and M. K. Seikel

J. Amer. Chem. Soc., 78, 825-829 (20 Feb. 1956)

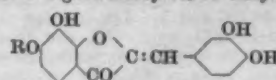
The pigments in the flowers of *C. maritima* are butein, coreopsisin, marein, luteolin-7-glucoside, and sulphurein. *C. gigantea* contains them all except the luteolin glucoside.

XII—Maritimein and Marein

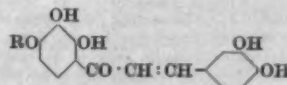
J. B. Harborne and T. A. Geissman

Ibid., 829-832

Maritimein is 6-glucosidoxy-7:3':4'-trihydroxyaurone—



and marein is 4'-glucosidoxy-2:3':3:4-tetrahydroxy-chalkone—



(R in both cases = glucosyl).

XIII—Ultraviolet Absorption Spectra of Phenolic Plant Pigments. Polyhydroxyaurones

T. A. Geissman and J. B. Harborne

Ibid., 832-837

Measurement in both alkaline and neutral solution of twenty-seven hydroxylated or methoxylated aurones shows that presence of a 4-, 3', or 5-hydroxyl in a 6-hydroxyaurone does not appreciably alter the spectra, but that a 6-hydroxyl group has a pronounced hypsochromic effect on aurone spectra. In presence of 6-hydroxyl the 2', 4'- and 7-hydroxyl groups are bathochromic, as is the 3' in presence of 4'. This is partly caused by cross-conjugation. C.O.C.

Chemical Constitution of Digitolutein, the Yellow Pigment of *Digitalis*

M. M. Janet, J. Chabasso-Massonneau, P. de Graeve, and R. Goutarel

Bull. Soc. chim. France, 108-133 (1955);*Chem. Abs.*, 50, 924 (25 Jan. 1956)

Digitolutein is shown to be 1-methoxy-2-hydroxy-3-methylantraquinone. C.O.C.

Chromate Pigments for Metal Protection

H. G. Cole

Chem. and Ind., 151-153 (3 March 1956)

Report of a lecture, partly historical, and of the ensuing discussion. C.O.C.

PATENTS**Solid Diazonium Salts**

General Aniline

USP 2,707,181

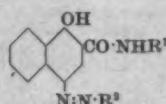
An aryldiazonium salt produced in aqueous soln. is precipitated as such or as the double salt formed by adding an inorganic complex-forming compound, e.g. ZnCl_2 . It is separated as a moist paste from the main liquor by either filtration, decantation, or centrifuging. This paste is slurried with a volatile water-immiscible inert organic solvent, and an inert water-absorbent salt, e.g. anhydrous MgSO_4 , is added to the slurry. The slurry is then filtered or centrifuged, and dried. An inert solid diluent can be added during drying to bring the strength of the diazonium salt compound to standard. The product has improved stability and purity, and yields brighter dyeings or prints when coupled than hitherto available products. C.O.C.

Coloured 1-Hydroxy-2-naphthamide Colour Couplers

Eastman Kodak Co.

USP 2,706,684

Compounds of formula—



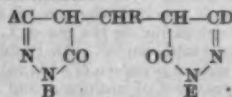
(R^1 = mononuclear Ar substituted *ortho* to the amide group with either Hal, alkoxy, or mononuclear aryloxy; R^2 = mononuclear Ar), e.g. 1-hydroxy-4-(2':5'-dibutoxy)-phenylazo-2-naphthamide, are colour couplers which on development yield a cyan dye image in the exposed portions with a background of magenta-coloured coupler in the unexposed areas serving as a colour-correcting image. C.O.C.

Bispyrazolone Colour Couplers

Eastman Kodak Co.

USP 2,706,683

Compounds of formula—



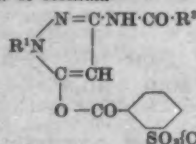
(R = subst. or unsubst. Ar of the benzene series; A, B, D, and E = H, Alk, subst. or unsubst. Ar, amino, or cycloamino, at least two of them being different), e.g. α -{4[(1':2':4':6'-trichlorophenyl)-3-{3''(2'':4'':di-*tert*-amylphenoxyacetamido)benzamido]-5-pyrazolonyl}] 1-phenyl-3-methyl-4-*p*-methoxybenzyl-5-pyrazolone, are colour couplers which split at the moment of coupling to yield two fragments which react with the developer oxidation product at approximately equivalent rates. C.O.C.

3-Acylamino-5-*m*-sulphobenzoyloxypyrazole Colour Couplers

Eastman Kodak Co.

USP 2,706,685

Compounds of formula—



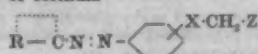
(R^1 = mononuclear subst. or unsubst. Ar of the benzene series; R^2 = mononuclear or aralkyl or aryloxyalkyl group of the benzene series or mononuclear arylene, e.g. the pyridinium salt of 1-(2:4:6-trichlorophenyl)-3-[*m*-(α -(2:4-di-*tert*-amylphenoxy)-acetamido)benzamido]-5-*m*-sulphobenzoyloxypyrazole, are excellent colour couplers whose solubilising groups are readily eliminated during development. C.O.C.

Colour Couplers

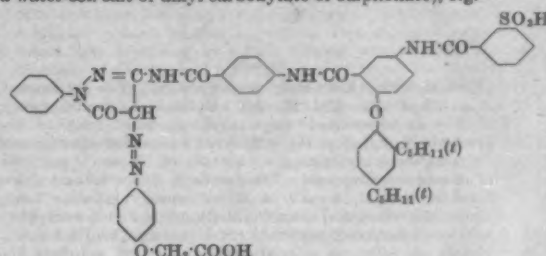
Kodak

BP 745,545

Compounds of formula—



(R = atoms to complete a 5-pyrazolone ring or a 1-hydroxy-phenol or -naphthol, the C atom being in the 4 position; X = O or a single bond; Z = COOH , SO_3H , or a water-sol. salt or alkyl carboxylate or sulphonate), e.g.—



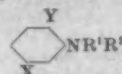
are used as photographic colour couplers. C.O.C.

Disperse Monoazo Dyes from 2-Amino-6-alkyl(or allyl)sulphonylbenzothiazole

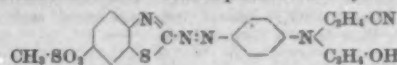
Eastman Kodak Co.

BP 744,877

Scarlet, violet, blue, and in particular bright red disperse dyes for cellulose acetate, nylon, etc. are made by coupling a diazotised 2-amino-6-alkyl(or allyl)sulphonylbenzothiazole with suitable *N*-substituted derivatives of aniline—



(R^1 and R^2 = Alk, hydroxyalkyl, cyanoalkyl, fluoroalkyl, etc., and R^3 may = H; X and Y = H, Hal, Alk, etc.). Thus, 2-amino-6-methylsulphonylbenzothiazole dissolved in 50% aq. H_2SO_4 is diazotised at below -3°C . with a solution of sodium nitrite in H_2SO_4 , and coupled with a soln. in 10% H_2SO_4 of *N*- β -cyanoethyl-*N*- β -hydroxy-ethylamine at -5°C . The sulphate of the dye—



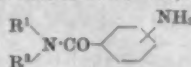
separates, and is filtered off and hydrolysed to the free dye by stirring with a large volume of water. It dyes cellulose acetate brilliant red. E.S.

Yellow Azoic Dyes for Cellulose Acetate and Nylon

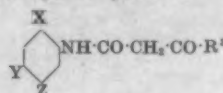
FH

BP 745,830

The diazotisable amines of BP 719,287—



(the benzene ring may contain Hal, or Alk, alkoxy, or aryloxy groups; R^1 , R^2 = H, Alk, aryl, aralkyl, or cycloalkyl, but neither must be H if the NH_2 and amide groups are *ortho* to one another) are applied to acetate rayon or nylon along with acylacetarlamides—



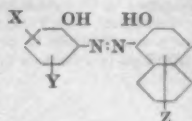
(R^3 = Alk or Ar; X = Alk or O-Alk; Y = O-Alk or Hal; Z = Alk, O-Alk, or Hal, with the proviso that Y = Hal and Z = Alk or O-Alk, or Y = O-Alk and Z = Hal, if X = O-Alk, and that Y = Hal and Z = O-Alk if X = Alk) and developed with nitrous acid to produce yellows fast to cross-dyeing. Thus 3-amino-4-ethoxybenz-*n*-butylamide and the sodium salt of acetoacet-4-chloro-2:5-dimethoxyanilide are applied to cellulose acetate from a slightly alkaline bath at 75°C . The fibre is then treated in cold nitrous acid and developed at 60 – 80°C . in a slightly alkaline bath to a reddish yellow. E.S.

Metal(Cobalt and Chromium)-complex Monoazo Dyes for Wool, Nylon, etc.

Ciba

BP 745,641

Sulphonamides of *o*-aminophenol are diazotised and coupled with β -naphthol and its derivatives to give monoazo compounds—



(X = H, NO₂, Alk, Hal, or acylamino; Y = sulphonyl; Z = Alk, O-Alk, Hal, H, or a sulphonic acid ester group; if Y = unsubstituted sulphonyl, at most one of the symbols X and Z = H), which are converted into Co and Cr complexes containing < 1 atom of Co or Cr per mol. of monoazo compound. The products dye wool and nylon from a neutral, weakly acid, or weakly alkaline bath. Thus, the monoazo compound 2-aminophenol-4-sulphonamide-6-bromo-2-naphthol (21.1 parts), dissolved in aq. NaOH at 80°C., is stirred with aq. cobalt sulphate (50 parts of 3.25% Co content). The cobalt-complex formed dyes wool bordeaux from a weakly alkaline, neutral, or acetic acid bath.

E.S.

Metal-complex Azo Dyes

BASF

BP 745,479

By metallising *oo'*-dihydroxyazo, *o*-alkoxy-*o'*-hydroxyazo, and *o*-carboxy-*o'*-hydrazo compounds, having an SO₃H group *para* to an *o*-hydroxy or *o*-alkoxy group, in presence of polyhydric alcohols, polyhydroxy ethers, or polyethers HO-(CH₂-CH₂-O)_n-CH₂-CH₂-OH (*n* = integer from 1 to about 25), the *para* SO₃H group is split off, with formation in good yield of the metal complex. The process is of special significance for preparing metal complexes of dyes derived from *o*-naphthol and its derivatives as coupling components. The products are pigments, colouring matters for lacquers, and dyes for wool, nylon, etc. Thus, the monoazo compound 2-amino-5-nitro-phenol-1-naphthol-4-sulphonic acid is added at 130°C. to a solution of cobalt chloride in ethylene glycol. After 3 hr. at 130–135°C. the cobalt complex is salted out. It contains no SO₃H group, and dyes wool and nylon reddish blue from a neutral bath.

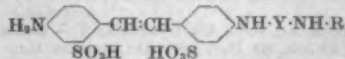
E.S.

Mono- and Dis-azo Stilbene Direct Dyes having an 8-Hydroxyquinoline Residue

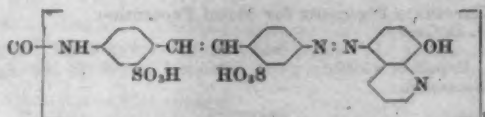
Ciba

BP 744,829

Direct dyes derived from 4-aminostilbene-2:2'-disulphonic acid containing 1 or 2 azo groups and 1 or 2 8-hydroxyquinoline residues, and capable of metallisation in substance, in the dye bath, or on the fibre, are made by the following general methods—(i) Tetrazotised 4:4'-diaminostilbene-2:2'-disulphonic acid is coupled with azo components at least one of which is an 8-hydroxyquinoline (I). (ii) 4-Amino-4'-nitro (or acylamino)stilbene-2:2'-disulphonic acid (II) is diazotised and coupled with an azo component, the nitro (or acylamino) group is converted into NH₂, and the product is diazotised and coupled with a further azo component; at least one of these azo components is I. (iii) Two molecules of II are condensed with 1 mol. of phosgene or a cyanuric halide, and the diamine formed by conversion of the nitro (or acylamino) groups into NH₂ groups is tetrazotised and coupled with suitable azo components. (iv) A compound—



(NH-R is the residue of a 4-amino-4'-hydroxyazobenzene-3'-carboxylic acid; Y = a triazine residue) is diazotised and coupled with I. Thus 2 mol. of 4-amino-4'-nitrostilbene-2:2'-disulphonic acid are condensed with 1 mol. of phosgene in presence of NaOH and sodium acetate. The dinitro compound so formed is reduced with iron and acetic acid to the diamine, which is tetrazotised and coupled with 2 mol. of 8-hydroxyquinoline in presence of NaOH and soda ash, to give—



which dyes cellulose fibres red-orange by the single- or two-bath aftercoupling process.

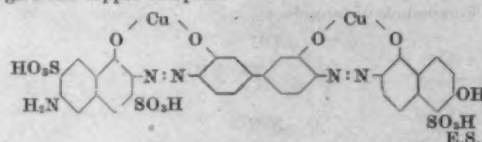
E.S.

Blue Metal(Copper)-complex Disazo Direct Dye

ICI

BP 744,930

The disazo compound obtained by coupling tetrazotised *o*-dianisidine (I) with 1 mol. of 1:6-dihydroxynaphthalene-5-sulphonic acid (II) and 1 mol. of 2-amino-5-naphthol-3:7-disulphonic acid (III) under alkaline conditions is converted into its copper complex under conditions which dealkylate the O-CH₃ groups, to give a blue direct dye whose good light fastness is maintained when dyeings made with it are given a crease-resistant finishing treatment, e.g. with urea-formaldehyde resins. Thus I is tetrazotised and, after almost neutralising with soda ash, a soln. of III in aq. soda ash is added. After 30 min. a soln. of the sodium salt of II in aq. ammonia and pyridine is added. The disazo dye so formed is then heated for 18 hr. at 90–95°C. with ammoniacal copper sulphate to give the copper complex—



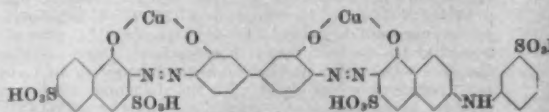
E.S.

Blue Metal(Copper)-complex Disazo Direct Dyes

ICI

BP 745,082

The disazo compounds prepared by coupling tetrazotised 3:3'-dimethoxy (or diethoxy)benzidine with 1 mol. of 1-naphthol-3:6-, -3:7-, or -3:8-disulphonic acid and 1 mol. of *N*-m-sulphophenyl-J acid (I) are converted into copper complexes with dealkylation of the methoxy or ethoxy groups. The products are blue direct dyes, of superior fastness to washing and to the effect of applying a crease-resist finish, and give less staining on cellulose acetate than the similar dyes of BP 352,956 (J.S.D.C., 47, 360 (1931)), which specifies the use of J acid and its derivatives without including the use of I. Thus *o*-dianisidine is tetrazotised and coupled with 1 mol. of 1-naphthol-3:6-disulphonic acid in presence of soda ash and then with 1 mol. of I in presence of ammonia and pyridine. The disazo compound is then heated at 90–95°C. for 18 hr. with ammoniacal copper sulphate to give the copper complex—



which dyes viscose rayon bright reddish blue.

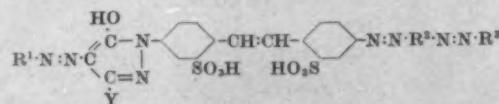
E.S.

Metal(Copper)-complex Trisazo Stilbene Direct Dyes

Ciba

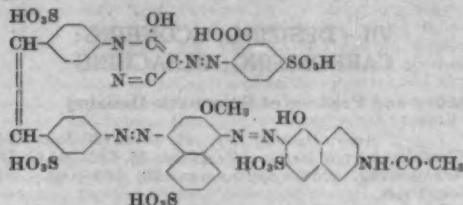
BP 744,666

The copper complexes of trisazo compounds—



(R¹ = aryl of benzene series having OH, O-Alk, or COOH *ortho* to the azo link; R² = residue of benzene or naphthalene series in which the azo groups are *para* to each other, and which contains *ortho* to the N:N-R² group OH or O-Alk; R³ = aryl having OH *ortho* to the azo link; Y = CH₃ or COOH) are grey to olive-green direct dyes of good fastness to light and crease-resist finishing treatments, e.g. with urea-formaldehyde resins. Thus, 5-sulphoanthranilic acid is diazotised and coupled

in presence of NaHCO_3 with 1-(4'-aminostilbene(4'))-3-methyl-5-pyrazolone-2':2''-disulphonic acid, and the aminomonoazo compound so formed is diazotised and coupled with 2-methoxy-1-naphthylamine-6-sulphonic acid in presence of acetic acid, which is gradually neutralised with soda ash. The aminodisazo compound so formed is then diazotised and coupled with *N*-acetyl-J acid in presence of NaHCO_3 and pyridine, to give the trisazo dye—



The copper complex, containing 2 Cu per mol. of trisazo compound, is formed by refluxing with copper sulphate and sodium acetate; it dyes cotton olive green. E.S.

Finely Divided Pigmentary Silica

Columbia-Southern Chemical Corp.

BP 745,822

An acid is added to an aqueous alkali-metal silicate (10–150 g. SiO_2 per litre), in presence or absence of a non-reactive alkali-metal salt, to bring the mixture to pH > 5. The product contains 90% by wt. of SiO_2 (when anhydrous), 2–10% of bound water, and 2–10% of free water. Its surface area is 25–200 sq.m./g. (determined by the Brunauer-Emmett-Teller method) and average ultimate particle size < 1 μ .

BP 745,890

The tendency for the surface area to increase unduly in acid medium is eliminated by heating the precipitated silica in aqueous medium at > 50°C. for < 30 min. C.O.C.

Hydrophobic Organophilic Pigments

American Cyanamid Co.

BP 745,865

Pigments are rendered suitable for lithographic inks by coating them with 0.5–20.0% of a high-mol.wt. pyridinium chloride, e.g. cetylloxymethylpyridinium chloride. C.O.C.

Pelleting Carbon Black (I p. 247)

Effect of Acids, Alkalies, and Salts on the Colour of Blue Anthraquinone Acid Dyes (VIII p. 255)

Classification of Direct Dyes by their Dyeing Properties on Viscose Rayon (VIII p. 255)

Use of Azo Dyes as Reagents in Inorganic Analysis and as Antibacterials—I (XIV p. 259)

Artificial Food Colourings and their Determination (XIV p. 259)

Polarography of the Monoximes and Dioximes of Benzoquinone, Naphthaquinone, and Anthraquinone (XIV p. 260)

V—PAINTS; ENAMELS; INKS

PATENT

Chlorinated Rubber as Undercoating for Polyvinyl Acetate Paint

Wright Stephenson & Co.

BP 745,349

Use of an undercoating based on chlorinated rubber greatly increases the adhesion of polyvinyl acetate paints to many surfaces, especially those exposed to weathering. C.O.C.

Chromate Pigments for Metal Protection (IV p. 251)

VI—FIBRES; YARNS; FABRICS

Photochemical Degradation of Jute—I

W. G. Macmillan and H. P. Bhattacharjee

J. Indian Chem. Soc., 32, 731–735 (Nov. 1955)

Jute is progressively degraded by exposure to a carbon-14 Fade-Ometer for times up to 100 hr., resulting in increased solubility in water and alkali and decreasing pH and acetyl content of the aqueous extract. The yields of holocellulose and of α -cellulose, together with the D.P. of

the α -cellulose, also decrease; and the copper No. of the jute, but not that of the isolated holocellulose, increases with increasing time of exposure. It is concluded that considerable degradation of lignin occurs, producing reducing substances (possibly polyhydric phenols). A.J.

Relation between Wool Felting and Single-fibre Properties

A. K. van der Vegt and G. J. Schuringa

Text. Research J., 26, 9–16 (Jan. 1956)

Apparatus is described for the measurement of single-fibre frictional constants and elasticity of fibres in certain solutions relative to that in water. Two series of experiments are described in which felting was studied as a function of the applied hydrodynamic force *P* for worsted yarns in which (a) frictional properties were modified by chemical treatments and (b) elasticity of the fibres was modified by immersion in aqueous solutions of salts and non-electrolytes. When *P* is less than the with-scale frictional resistance *R₁*, no shrinkage occurs. For higher values of *P*, rate of shrinkage is proportional to (*P*–*R₁*) and inversely proportional to the Young's modulus of the fibre. When *P* exceeds the anti-scale frictional resistance *R₂*, shrinkage becomes almost independent of *P*. J.C.F.

Conversion of Phenylalanine into Tyrosine in the Silkworm Larva (*Bombyx mori*)

T. Fukuda

Nature, 177, 429–430 (3 March 1956)

Phenylalanine, labelled with ^{14}C , was injected into silkworms, which later spun radioactive cocoons. The fibroin, after degumming and solvent extraction, was hydrolysed in HCl, and tyrosine, alanine, and glycine were isolated from the hydrolysate. The tyrosine showed high radioactivity, and is assumed to be synthesised from phenylalanine *in vivo*. A.J.

Intermolecular Forces in Polyamide Fibres

A. Parisot

Bull. Inst. Text. France, (54), 7–38 (June 1955);

Melliand Textilber., 37, 65–75 (Jan. 1956)

A study of the properties of long-chain fatty amides suggests that the amide group acts as a centre of rigidity in the hydrocarbon chain (because of partial double-bond character of the C–N link), and in addition transmits a certain degree of rigidity to the parts of the hydrocarbon chain in its immediate vicinity. The total rigidity of the polymer chains in a polyamide (which determines the m.p.) may be analysed into four components—(a) the (small) intrinsic rigidity of the hydrocarbon chain; (b) the contribution of each amide group; (c) the contribution from resonance interaction between amide groups in adjacent chains; and (d) additional rigidity induced when amide groups in the same chain are sufficiently close together. These considerations lead to a classification of polyamides which agrees with that based on m.p. and polymerisation pattern. J.C.F.

Electrical Charge on Individual Fibres

C. E. Moesman and E. Rideal

Canadian J. Chem., 34, 88–93 (Jan. 1956)

The fibre is fixed horizontally to a quartz torsion suspension so that the fibre is immersed in a soln. midway between a pair of parallel platinum-foil electrodes. On applying a potential the fibre is deflected to the appropriate electrode, the angle of deflection increasing with increasing voltage. The system is reversible. Terylene fibres have a negative charge in H_2O and dil. HCl but positive in dil. $\text{Th}(\text{NO}_3)_4$. In soln. of anionic detergents, e.g. sodium dodecyl sulphate, the negative charge increases at very low concn. of detergent (ca. 4×10^{-6} M.), but decreases with increasing concn. It is not possible, using this technique, to measure the fibre charge quantitatively. A.J.

Properties of Asbestos. I—Colloidal and Surface Chemistry of Chrysotile

F. L. Fudzsack

J. Phys. Chem., 59, 892–895 (1955)

PATENTS

Pigmentation of Viscose

Kuhlmann

USP 2,706,689

A concentrated suspension of the pigment in an aqueous solution of a cellulose polyalcohol ether and dil. aq. NaOH is added to the viscose. Thus lampblack (5 kg.)

is added to an alkaline aq. solution of glycolcellulose (4% glycolcellulose and 5% NaOH in 100 litres). This yields an extremely fine dispersion, which can be stored for several months without settling out. It is used for colouring viscose grey or black. C.O.C.

Imparting Affinity for Acid Dyes and Decreased Water Absorption to Cellulose Material by treating with Guanamine Resins

American Cyanamid Co. USP 2,706,718

The materials are treated with a guanamine-formaldehyde resin, e.g. acetoguanamine (1250 parts, 10 mol.), formalin (3240, 40 mol.) and 2N-NaOH (22) are heated to reflux in 30 min., refluxed for 30 min., 2N-NaOH (19) added, filtered, brought to pH 8 and spray-dried at 270–280°C. A 5% aqueous solution of the product (170) is added to cellulose xanthate (8.5% cellulose) (2,000), which is then spun in the usual manner within 2 hr. of the resin addition. The resulting fibre is washed with water, treated with 0.25% aq. diammonium hydrogen phosphate and heated for 25 min. at 150°C. C.O.C.

Regenerated Protein Fibres

ICI

BP 742,890

The loss in strength caused by dyeing under acid conditions is reduced when the regenerated fibre is heated with acidified formalin at 140–180°C. W.G.C.

Improving the Elasticity, Water-repellency and Wet Heat Resistance of Polyvinyl Alcohol Fibres

Kurashiki Rayon Kabushiki Kaisha BP 745,219

The fibres are first given a heat treatment and are then treated with aldehydes or ketones of > 3 C or with their acetals formed with alcohols of < 4 C. Heat and wet resistance are most effectively improved by treatment with HCHO and decrease slightly when higher aldehydes are used, but the latter improve the elasticity considerably and the water repellency most markedly. C.O.C.

Delustred Polyamide Filaments

Vereinigte Glanzstoff-Fabriken

BP 745,182

Modification of BP 733,007 (J.S.D.C., 71, 560 (Sept. 1955)). High bulk-elasticity with simultaneous delustring is obtained by adding polystyrene of mol. wt. > 100,000 to the monomer. C.O.C.

Metallic Compounds of Polyesters for producing Filaments, etc.

Chemische Werke Albert

BP 745,142

Polyesters are treated before, during or after extrusion with an alkoxide or an alkoxo salt of a di- or higher-valent metal (except alkaline-earth metals, which are unsatisfactory) or with a resin formed by treating such a compound with a tautomerically-reacting compound containing keto-enolic groups e.g. those described in BP 718,283 and 718,284. This results in the metal in these compounds or resins combining chemically with the polyesters. C.O.C.

Acrylonitrile Copolymers

Distillers Co.

BP 744,933

The copolymers of acrylonitrile with an ester or ether of *m*-isopropenylphenol are useful in the production of fibres of good dyeability. W.G.C.

Acrylonitrile-Polyvinyl Alcohol Grafted Polymers

ICI

BP 742,900

Yarns of improved wet strength are produced by treating polyvinyl alcohol with < 40% of acrylonitrile to form a "grafted polymer" and spinning the resulting viscous solution into a salt solution. W.G.C.

Linear Polyesters of Sulphonyldibenzoic Acids

Kodak

BP 744,975

Linear polyesters having high melting or softening points are obtained by heating a *mm'*-, *mp'*-, or *pp'*-sulphonyldibenzoic acid, or its alkyl or β -hydroxyethyl diester, with a straight-chain polymethylene ω -glycol. W.G.C.

Metal-coated Glass Filaments

Owens-Corning Fibreglass Corp.

BP 745,279

Molten glass is continuously drawn from a container downward into filaments which pass closely against an orifice which leads by way of a horizontal passage to a bath of molten metal. The pressure of the metal is sufficient to ensure that a blob protrudes out of the orifice, which

may be so constructed that the metal does not wet it. The filaments pass down through the blob and are thus coated with the metal. J.W.B.

Stabilised Acrylonitrile Polymers and Copolymers (XIII p. 259)

Electron Microscopy of Fibres (XIV p. 260)

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

Theory and Practice of Enzymatic Desizing

J. Voss

Amer. Dyestuff Rep., 45, 58–63 (30 Jan. 1956)

Translated from *Melliand Textilber.*, 35, 762–764 (July), 876–880 (Aug. 1954); see J.S.D.C., 70, 469 (Oct.), 518 (Nov. 1954).

Effect of Long-chain Alcohols on the Properties of Sodium Laurate Solutions

I—Surface Tension

O. Harva

Rec. Trav. chim., 75, 101–111 (Feb. 1956)

The surface tensions of sodium laurate solutions containing aliphatic alcohols from hexanol to decanol have been measured at pH 11 and 24°C. The break points which occur, in all cases, in the surface tension-concentration curves at the higher alcohol concentrations are attributed to the formation of a complex between the laurate anion and the alcohol molecule, the process resembling a chemical reaction, and following the law of mass action.

II—Critical Micelle Concentration

Ibid., 112–116

The effect was studied of monohydric alcohols from hexanol to decanol and of the dihydric alcohols 1:2-decanediol and 1:10-decanediol on the critical micelle concentration (C.M.C.) of sodium laurate in aqueous solution at pH 11 and 24°C. Break points in the C.M.C.-alcohol concn. curves were observed with all the monohydric alcohols and with 1:2-decanediol, and were attributed to complex formation between the laurate anion and the alcohol molecule. When, however, complex formation does not occur, as is considered to be the case with 1:10-decanediol, the relationship between C.M.C. and diol concn. is linear up to the saturation concn. of the diol. W.K.R.

Rationalisation of Hypochlorite Bleaching

G. I. Fridlyand

Nauch.-issledovatel. Trudj Tsentral. Nauch.-issledovatel.

Inst. Lubyanykh Volokon, 7, 147–163 (1953):

Referat. Zhur. Khim., 45553 (1954):

Chem. Abs., 50, 578 (10 Jan. 1956)

Greatest degradation of cellulose occurs when the hypochlorite liquor is at pH 6.5–7.5, the least at pH 9.5–11.0. C.O.C.

Rationalisation of Linen Bleaching

O. E. Itina

Nauch.-issledovatel. Trudj Tsentral. Nauch.-issledovatel.

Inst. Lubyanykh Volokon, 7, 163–177 (1953):

Referat. Zhur. Khim., 45555 (1954):

Chem. Abs., 50, 577 (10 Jan. 1956)

A satisfactory bleach is obtained by, given an alkali boil, treatment with NaOCl and then with H₂O₂ in presence of an antichlor. The optimum concn. of active O in the H₂O₂ bath is 0.4–0.43 g./litre; the liquor should be at 87–90°C., time of treatment 2 hr., and the liquor ratio 10 : 1. It should be made alkaline with 6–10 g. Na silicate per litre. C.O.C.

PATENT

Dry Cleaning

H. Kreussler

BP 745,195

Addition to the solvent of a substance which flocculates or aggregates the dirt considerably improves the cleansing of the goods. Such substances may be water-soluble, e.g. sodium or potassium phosphates, swellable in water, e.g. carboxymethylcellulose, or water-insoluble, e.g. activated carbon. C.O.C.

VIII—DYEING

Spectral Regions of Daylight which cause Fading
K. McLaren

J.S.D.C., 72, 86-90 (March 1956)

Organic colouring matters are faded by absorbed ultraviolet and visible radiation up to a critical wavelength, above which radiation is non-actinic even if strongly absorbed. This wavelength is generally related to the normal light fastness of the colouring matter, "normal" referring to the substrate for which it was originally developed, e.g. vat dyes on cotton, disperse dyes on acetate rayon. The critical wavelength decreases as the resistance to fading increases, being in the red when the light fastness is 1-2 (minimum) and in the blue when it is 6-8 (maximum); there are, however, some exceptions to this rule.

As long-wave radiations preponderate in daylight and as the absorption bands are usually strongest in the visible spectrum, fugitive organic colouring matters are mainly faded by visible light, whilst those of high normal light fastness can in general be faded only by ultraviolet, violet, and blue light.

The differences between the composition of actinic radiation constituting daylight and that emitted by the enclosed carbon arc have been shown to be relatively unimportant as a possible source of gross anomalies in light fastness testing based on comparison with light fastness standards. These differences do, however, render meaningless any attempt to equate one hour's lamp exposure with so many hours' sunshine. AUTHOR

Pigment Dyeing

M. Domingo Ferré

Ingeniería Textil, 23, 24-29 (Jan.-Feb. 1956)

The preparation of the goods, physical state of the vat dye, and methods of dyeing and developing are briefly discussed. S.R.C.

Effect of Acids, Alkalis, and Salts on the Colour of Blue Anthraquinone Acid Dyes

R. H. Peters and H. H. Sumner

J.S.D.C., 72, 77-86 (March 1956)

Certain blue anthraquinone acid dyes show colour changes when the dyed material is treated with acid, alkali, or salt. For eight dyes, these properties have been correlated with the changes which occur when these reagents are added to solutions of the dyes in water. Addition of acid to the dye solution gives a salt by reaction with amino groups in the dye. This results in a reduction of the intensity of the absorption band characteristic of the blue colour and produces one at shorter wavelengths. These changes have enabled the dissociation constants to be calculated, and the latter run parallel with results of acid treatment of dyed patterns. Alkali, on the other hand, reacts with any hydroxyl groups present, giving rise to a colour change. Here it is not possible to calculate the dissociation constants, but the spectral changes in solution agree with the colour changes on the fibre. Addition of salt to solutions of these dyes does not produce a wavelength change but merely a reduction in intensity, presumably due to aggregation. This effect is in agreement with the changes which occur on salt spotting. Another factor is that the salt solution may cause desorption of the dye from the fibre, and hence migration can occur. The susceptibility of a dyed fibre to salt spotting has been shown to parallel the ability of the dye to be desorbed as measured by the affinity of the dye for the fibre. AUTHORS

Classification of Direct Dyes by their Dyeing Properties on Viscose Rayon

A. I. Avrumina and A. I. Goloviehkina

Nauch.-issledovatel. Trudŭ Tsentral. Nauch.-issledovatel.

Inst. Shelk. Prom., 59-67 (1953):

Referat. Zhur. Khim., 45561 (1954):

Chem. Abs., 50, 575 (10 Jan. 1956)

Twenty-one Russian dyes are divided into four classes by means of their dyeing properties for viscose rayon. The first group (Direct Light Blue, Direct Turquoise Light-resistant, and Direct Light Blue Z) have little affinity for the fibre in absence of electrolytes, neither temperature nor time of dyeing having much effect on absorption. The second group (Direct Violet, Direct

Green ZhKh, Direct Ruby Red, Direct Red X, Direct Maroon, Direct Brown ZhKh, Direct Brown KKh, Direct Blue Light-resistant, and Direct Dark Green) show appreciable absorption at the start of dyeing, absorption increasing with increase of temperature to a sharp maximum at approx. 80°C., and they level satisfactorily. To prevent spottiness in the early stages of dyeing, the electrolyte should be added in 3-4 lots during the first 20 min. of dyeing. The third group (Direct Blue KM, Direct Blue M, Direct Black ZS, Direct Bright Orange, Direct Blue ZM, Direct Black Z, and Direct Black K) have good affinity in absence of electrolytes, there is sharp increase in exhaustion with rise in temperature, and they level poorly. They should be dyed with 5% NaCl, and the temperature should be only gradually raised. The fourth group consists of Chrysophenine, which has an optimum dyeing temperature of 40-60°C. It exhausts satisfactorily in absence of electrolytes and gives 75% exhaustion when they are present; it levels well and gives good results in combination with dyes of the first group. C.O.C.

Sequestering Agents in Wool and Cotton Dyeing

H. E. Millson

Amer. Dyestuff Rep., 45, P 66-P 81 (30 Jan. 1956)

Characteristics and mode of operation of sequestering agents are briefly discussed. Metals are liable to be present in wool for a number of reasons, and are particularly likely to be concentrated near the tips, thus leading to tippy dyeing. This is well illustrated photographically by including radioactive ⁶⁰Co in a dye bath; the effect almost disappears in presence of the ethylenediaminetetra-acetate reagent, which chelates the offending metal. Spectrophotometric studies are made on the effects of metal ions and chelating agent on dyeings of a very large selection of dyes. Effects on the fastness are also studied, and results are tabulated in detail. Copper-complex direct cotton dyes are investigated with respect to subsequent rubberisation; it is found that addition of agent effectively prevents any free metal ions (including Cu or Mn from water supplies) being left in the material and causing trouble later. J.W.B.

Influence of Different Mordants on the Dyeing of Rabbit Hair with Ursols

F. Stather, S. Walther, and U. Stather

Gesammelte Abhandl. deut. Lederinst. Freiburg/Sa.,

(12), 82-86 (1955):

Chem. Abs., 50, 1318 (25 Jan. 1956)

Untreated rabbit hair and samples treated with K₂Cr₂O₇ and acetic acid; K₂Cr₂O₇, acetic acid, and Na acetate; K₂Cr₂O₇ brought to pH 7 (monochromate); FeSO₄ and acetic acid; were dyed with Ursols. Cross-sections of the dyed hairs showed that no dye was taken up by the untreated hair, with FeSO₄ only the medulla was coloured, with Cr the cortex was coloured, both penetration and intensity of coloration being obtained at pH 4. To get good penetration through the cortex it is better to add the H₂O₂ after 45 min. rather than at the start of dyeing. C.O.C.

Barrel Anodising and Dyeing of Small Aluminium Articles

C. Etienne

Electroplating and Metal Finishing, 8, 359-363 (1955):

Chem. Abs., 50, 701 (25 Jan. 1956)

The following are discussed—packing, gassing, surface preparation, anodising, rinsing and neutralising, dyeing, and sealing. C.O.C.

PATENTS

Dyeing Hair and other Keratinous Fibres

Gillette Industries

BP 745,144

Treatment of hydroxybenzene compounds with tyrosinase causes aerobic oxidation to introduce a hydroxy group *para* to the existing hydroxy group. In the case of monohydroxybenzenes two hydroxy groups are introduced into the nucleus, one of them going into the free *ortho* position. This is made use of in hair dyeing by treating the hair first with an aqueous solution of mono- or *o*-dihydroxybenzene or an alkyl derivative thereof having an unsubstituted position *para* to a hydroxy group or in the case of the monohydroxy compounds having an unsubstituted position *ortho* to the hydroxy group and an unsubstituted position *para* to either the hydroxy group or the unsubstituted *ortho* position. The hair is simultaneously

or subsequently treated with tyrosinase. Thus grey human hair is dyed brown by treating with catechol (0.11 g.) in water (10 ml.) to which has been added 5 ml. of a very dilute extract of tyrosinase, and exposed to the air for 30 min. In another example wool cloth is dyed a deep yellowish brown fast to repeated washing by impregnating it with a solution made up of *p*-cresol (0.11 g.), sodium dihydrogen phosphate (0.08 g.), disodium hydrogen phosphate (0.18 g.), water (10 ml.) and dilute tyrosinase (1 ml.) and then air-oxidising for 30 min.

BP 745,531

The hair is treated with an aqueous solution of 2:4:5-trihydroxytoluene and then with an aliphatic or aryl-aliphatic amine at pH 5–12 in absence of sulphites, hydro-sulphites or mercaptans. Thus grey human hair, saturated with a solution at pH 10.5 made up of 2:4:5-trihydroxytoluene (0.07 g.), *n*-butylamine (0.07 g.), Na_2CO_3 (0.11 g.) and water (10 ml.) and air-oxidised for 30 min., rinsed and washed, was dyed a light golden brown fast to further washing. Wool cloth saturated with 2:4:5-trihydroxytoluene (0.14 g.), cyclohexylamine (0.10 g.), Na_2CO_3 (0.11 g.) and water (10 ml.), air-oxidised for 30 min. and washed was dyed a medium brown fast to washing.

C.O.C.

Structure of Dithionite (III p. 248)

Pigmentation of Viscose (VI p. 253)

IX—PRINTING

Colour Changes in Colour Photographs on Ageing

F. Lieber

Bild und Ton, 8, 105–106 (1955):*Chem. Abs.*, 50, 708 (25 Jan. 1956)

The image on an Agfacolor reversal film rolled up with interleaving tissue and stored for 10 years turned blue. The image had been partly transferred on the paper with yellow as the dominant colour.

C.O.C.

Colour Changes in Colour Photographs on Ageing

K. Meyer

Bild und Ton, 8, 158–159 (1955):*Chem. Abs.*, 50, 708 (25 Jan. 1956)

The yellow image seen by Lieber (see preceding abstract) consists of oxidised developer. Azomethine dyes tend to hydrolyse in presence of moisture. The yellow dye is particularly susceptible to hydrolysis, with formation of developer and a non-diffusing ketone. The developer diffuses into the paper and is oxidised by atmospheric oxygen. The readily hydrolysed yellow dye of Gevacolor positive film can be stabilised by hardening the gelatin with formaldehyde.

C.O.C.

PATENTS

Pigment Printing

FBY

BP 745,356

Excellent results are obtained by using an emulsion of a water-insoluble copolymer of a vinyl compound containing reactive H or Hal atoms and an acrylate or methacrylate of an alcohol of > 3 C or a butadiene or chlorobutadiene. Thus 1:1-dichloroethylene (70 parts) and α -chlorobutyl acetate (30) are emulsified in a 2% aqueous solution of the Na salt of the sulphonic acids obtained by sulphochlorinating long-chain paraffins. As catalyst there is used a mixture of the Na salt of the sulphonic acids of long-chain paraffins (0.5) and $\text{N-H}_2\text{SO}_4$ (2). After heating at 20°C. for 20 hr. a 100% yield of a latex containing 39.5% of the copolymer is obtained. This latex (35) is stirred into a mixture of 25:100 alginate thickening (15) and turpentine (12) in presence of dimethylamine oleate as emulsifier. To the resulting paste is added Helio Fast Blue BL paste 20% (15) and 25% aq. hexamethylenediamine (15), the latter having been previously made weakly acid with acetic acid. Water is then added to bring to 100 parts. Prints obtained on cotton with this paste have, after baking at 140–145°C., a soft handle and excellent fastness to rubbing and washing.

C.O.C.

Preventing Formation of Prussian Blue Stain in Photographic Colour Prints developed and treated with a Ferrocyanide Bleach

Eastman Kodak Co.

USP 2,706,687

Decorating Ceramic or other Ware

F. Malkin & Co.

BP 746,070

A flexible endless band coated with the printing ink or paste is pressed against a stationary former (of approxi-

mately the same contour as the article to be coated) by a pad bearing the design to be coated. This causes the surface of the pad to be evenly coated with the ink or paste so that the pad is ready to be applied to the article to impress the design upon it.

C.O.C.

Structure of Dithionite (III p. 248)

Coloured 1-Hydroxy-2-naphthoamide Colour Couplers (IV p. 251)

X—SIZING AND FINISHING

Physical Properties of Chemically Modified Cottons

J. N. Grant

Text. Research J., 26, 74–80 (Jan. 1956)

A number of commercial varieties of cotton, selected to provide samples with a wide range of fibre properties, were chemically modified, in yarn form, by mercerisation, ethylamine decrystallisation, amination, carboxymethylation, acetylation, and cyanoethylation. Results of physical tests on yarns and single fibres of the original and modified cottons are given. The changes in physical properties depend on the type of treatment, the extent of reaction, and the tension on the yarn during treatment. The inherent fibre characteristics of the original samples exert an important effect on the properties of the modified cottons.

J.C.F.

Improved Weather Resistance by Acetylating Vat-dyed Cotton

W. N. Berard, S. G. Gremillion, and C. F. Goldthwait

Text. Research J., 26, 81–86 (Jan. 1956)

Cotton dyed with selected vat dyes which are fast to light and subsequently acetylated (ca. 18% acetyl) possesses greatly enhanced weather resistance. The combination of the two treatments has a much greater effect than either alone. Vat dyes which are recognised as promoting deterioration of cotton under ordinary conditions of exposure to sunlight are rendered less active by acetylation. Outdoor weathering tests indicate that the combined treatment may more than double outdoor service life compared with cotton vat-dyed only or acetylated only.

J.C.F.

Cyanoethylation of Cotton

J. Compton, W. H. Martin, B. H. Word, and R. P. Barber

Text. Research J., 26, 47–66 (Jan. 1956)

The chemical structure of cotton and the morphological features of the fibre are described, and the basis of the reaction between cellulose and acrylonitrile in the presence of aq. NaOH is outlined. The methods which have been studied as potentially suitable for the large-scale production of cyanoethylated cotton are—I Liquid-phase reaction: (a) caustic soln. pre-steep followed by liquid acrylonitrile; (b) caustic soln. dispersed in acrylonitrile. II Vapour-phase reaction: caustic soln. pre-steep followed by exposure to acrylonitrile vapour. These methods are described in detail, and the effects of variation of reaction conditions discussed. Cyanoethylation of cotton produces little alteration in the morphological structure, and the modified fibre, whilst retaining most of the desirable properties of cotton, is rot-proof, more resistant to degradation by heat and acid, and more resistant to abrasion in some uses, and possesses improved dyeing properties.

J.C.F.

One-step Process for the Cyanoethylation of Cotton

A. H. Gruber and N. M. Bikales

Text. Research J., 26, 67–73 (Jan. 1956)

A simplified one-step process for the partial cyanoethylation of cotton yarn and stock in the package-dyeing machine is described. A mixture of caustic solution and acrylonitrile is circulated through the packages at room temp. for 10 min. before heating to reaction temp. This preliminary cold circulation allows even distribution of caustic throughout the packages and ensures uniformity of reaction. Statistically designed experiments showed 2% aq. NaOH and a reaction time of 40 min. to be optimum conditions. These variables were held constant in further experiments in which the effects of reaction temp. and caustic solution : cotton ratio on degree of cyanoethylation and by-product formation were studied. Acrylonitrile may be recovered in good yield from the principal by-product, $\beta\beta$ -oxydipropionitrile, by catalytic dehydration.

J.C.F.

Properties of Cotton treated with β -Propiolactone

R. M. Reinhardt, J. D. Reid, and G. C. Daul

Text. Research J., **26**, 1-9 (Jan. 1956)

Cotton fabric and thread were treated with β -propiolactone (I) (a) in boiling xylene, and (b) in xylene at 20°C. after impregnation with 15% NaOH soln. The polymeric material formed impregnates the fibre, causing it to swell, and cannot be removed, even from the surface of the fibre, by solvents which dissolve polymerised I. This indicates that a graft polymer bound to the cellulose is formed. X-Ray investigation shows that at lower weight gains reaction by method (a) takes place in amorphous regions only. In (b) reaction occurs also in crystalline regions. Physical properties of treated samples show no improvement over controls. Resistance to rotting, heat, and simulated weathering is generally slightly better than that of controls. Cotton treated with I can be dyed with disperse as well as direct dyes.

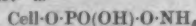
J.C.F.

Cellulose-Phosphate-Urea Reaction

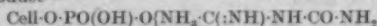
A. C. Nuessle, F. M. Ford, W. P. Hall, and A. L. Lippert

Text. Research J., **26**, 32-39 (Jan. 1956)

The cellulose-phosphate-urea reaction is of interest for the production of flameproof finishes on cellulosic fabrics. It is shown that when urea and phosphoric acid react with cellulose at temp. below 170°C., for such times that the urea remains molten throughout the reaction, the chief product is—



Other nitrogenous bases may replace ammonium; e.g. treatment of cotton with a melt containing guanidylurea phosphate and urea gives a fabric with satisfactory strength and durable flame-retardant finish. The N/P ratio corresponds to the product—



Under more drastic curing conditions more complex products are obtained. Most of the modified celluloses, particularly the ammonium types, show ion-exchange properties. The NH_4^+ radical may be replaced by metals, and also by hydrogen to give Cell-O-PO(OH)_2 .

J.C.F.

Deposition of Polyacrylonitrile in Wool. II—Properties of Wool containing Internal Deposits of Polyacrylonitrile

L. Valentine

J. Textile Inst., **47**, T1-T15 (Jan. 1956)

Wool containing internal deposits of polyacrylonitrile becomes less soluble in reagents which normally dissolve it, e.g. aqueous sodium sulphide or peracetic acid-ammonium hydroxide, the amount which dissolves decreasing almost linearly as the polymer content is increased. Rate of swelling is slightly reduced, but the limiting values are reduced much more and are reached in times only slightly greater than those for pure wool. There is only a slight Allwörden reaction. Elastic properties are virtually unaffected, though there may be small increases or decreases in work to stretch 30% according to the biological type of the fibre, no satisfactory explanation being found for this. The possibility of internal graft copolymers being formed between the polymer and the wool is discussed, and while no definite conclusion is drawn it is considered that the blend of polymer and wool must be intimate and not in the form of gross deposits. Abrasion resistance is only slightly increased, the maximum effect being produced with 20% deposit. Regain is lowered more than would be expected on the basis of simple dilution of wool by polymer, and the large effect with low depositions indicates that the polymer is interfering with specific moisture-adsorption sites. Moderate deposits markedly reduce the milling shrinkage, and in this respect polyacrylonitrile is much more effective than other vinyl polymers which have been previously studied. Removal of surface deposits does not affect this resistance, and neither scale masking nor alteration of elastic properties is capable of explaining the phenomenon.

J.W.B.

PATENTS

Crimped Thermoplastic Yarns

G. H. Heath & Co.

BP 743,906

Thermoplastic yarn is crimped by pulling over a sharp or scraping edge which is heated, with substantial change of direction at the edge and setting the yarn in the crimped condition.

W.G.C.

Crinkled Yarns

Moulinage et Retorderie de Chavanoz

BP 745,337

Crinkle yarns from e.g. polyhexamethylene-adipamide or polyacrylonitrile are produced by passing a yarn through a setting zone, in which heat is applied by contact with a hot body, by infrared radiation or by high-frequency heating, and then applying false twist to the yarn in a twisting zone after emergence from the setting zone. The yarn is unconfinned between the zones so that the twist feeds backwards into the yarn, where it becomes set, the set being removed again beyond the false-twisting zone.

J.W.B.

Imparting Dimensional Stability to Cellulose Fabrics

Cluett, Peabody & Co.

BP 744,991

The fabric is impregnated with an aqueous solution of the product obtained by treating a subst. or unsubst. pyruvic aldehyde or a dialdehyde with an amino-aldehyde or amino-aldehyde condensate, drying and baking. Thus glyoxal (120 g.) and dimethylurea (80 g.) were heated in water for 15 min. at 160°F. The solution was cooled to room temperature, oxalic acid (6 g.) added and the volume made up to 1 litre. Spun viscose rayon fabric was impregnated with its own weight of the liquor, dried at 212°F. and baked at 280°F. for 3 min. The treated fabric had a full, crisp and lofty handle with good draping properties and excellent resistance to crushing, creasing and shrinkage on repeated washing.

C.O.C.

Continuous Process for rendering Fabric Dimensionally Stable

Samco Holding Corp.

BP 742,430

The moist fabric is led longitudinally in successive loops through a treating zone. Each loop is supported at its upper and lower portions. The fabric in each loop is continuously advanced by withdrawing the fabric from the upper forward portion of each loop and feeding it to the upper rearward portion of the next loop. Preferably there is sufficient fabric in each loop to form several folds of fabric at the bottom of each loop, thus relieving it of all tension. Thus the fabric may be fed through a succession of J-boxes while being dried.

C.O.C.

Non-woven Fabric

Chicopee Manufacturing Co.

BP 745,065

A carded lap of oriented fibres has adhesive applied to it in an articulated multi-segmental pattern. The individual elongated segments of this pattern are separated from but hingedly connected by unbonded lengths of fibres. A good proportion of these segments are inclined obliquely to the direction of fibre orientation. This gives a fabric having a high degree of elasticity.

C.O.C.

Permanently Embossing Cotton Fabric

Heberlein & Co.

BP 745,117

The fabric has on it a pattern of a resin precondensate or is impregnated with the precondensate and then printed with an agent which inhibits curing of the resin. It is then embossed, baked to cure the resin, rinsed in water and finally treated with an alkaline or neutral swelling agent which has no shrinking or parchmentising action. Thus bleached cotton taffeta is printed with a paste made up of hexamethylolmelamine precondensate (175 g.), water (150), conc. ammonia (5), Tylose TWA, 50:100 (Kalle & Co.) (550), 1:1 aq. NH_4 thiocyanate (20), and Acramine Green B (FBy) (100). It is dried at 40°C., embossed at 200°C., baked for 4 min. at 140°C., rinsed and dried in the loose state. Finally it is padded with 20%Bé. NaOH, stored for some time, the NaOH rinsed out with hot and cold water, and the fabric tenter-dried. This yields an embossed green pattern on a smooth white ground.

C.O.C.

Reducing the Pilling Propensity of Fabrics containing Thermoplastic Synthetic Fibres

DuP

USP 2,706,845

The surface of the fibres in the exposed crown of the yarn is first disfigured by randomly flattening their cross-sectional dimensions and then locking them within the fabric structure by compression with adjacent fibres at the points of asperity. Thus the fabric is brushed gently with a rapidly revolving brush having bristles which give a heel-to-toe, non-plucking contact, the fabric then being shrunk to lock the fibres within the fabric.

C.O.C.

Coating Cotton Yarn or Fabric

Commonwealth Engineering Co.

USP 2,706,690

The material is treated with a solution of dextran so that the fibres are penetrated, alkylated in alkaline solution, dried and baked. The coated material is resistant to ordinary chemical attack but can be rendered tacky by use of a suitable solvent so that it can be caused to adhere to other materials.

C.O.C.

Permanent Setting of Human Hair or other Proteinaceous Fibre

National Lead Co.

BP 745,179

The fibre is treated with an ester of a compound of formula $HO-R^1-NR^2R^3$ (R^1 = ethylene or alkyl-substituted ethylene; R^2 = β -hydroxyalkyl or β -aminoalkyl; R^3 = H, Alk of 1-3 C, β -hydroxyalkyl, or β -aminoalkyl) with titanate or zirconic acid, e.g. β -aminoethylethanolamine titanate. This splits the disulphide bonds, which are reconstituted when the agent is washed off the fibre.

C.O.C.

Increasing the Adhesion of Synthetic Resins to Glass Fibres

Libbey-Owens-Ford Glass Co.

BP 745,374

Fibres treated with a true aqueous solution of an alkenyl-alkoxysilane and dried are given a coating which greatly improves the adhesion to them of synthetic resins, especially under high humidity conditions or when immersed in water.

C.O.C.

XI—PAPER AND OTHER CELLULOSIC PRODUCTS**Kinetics of Hydrolysis of Cellulose Fibres**

A. Meller

Chem. and Ind., 138 (18 Feb. 1956)

The view of Stewart and Williams (*ibid.*, 1350 (1955)) that the presence of fractions of different D.P. in cellulose fibres may give rise, in hydrolysis, to a series of apparent zero-order reactions is criticised. If this view is correct, then (a) the rate of loss in weight plotted against time of hydrolysis should give discontinuous horizontal lines and (b) the ratios of time values corresponding to equal fractional weight losses should be the same. On application of these tests to the data it appears that neither (a) nor (b) is substantiated. Statistical analysis shows that there is no evidence for the hypothesis that the relationship between loss in weight and time of hydrolysis is linear.

W.R.M.

Electron Microscopy of Fibres (XIV p. 260)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS**Evidence for a Reversible First-order Phase Transition in Collagen-Diluent Mixtures**

R. R. Garrett and P. J. Flory

Nature, 177, 176-177 (28 Jan. 1956)

The volume-temperature behaviour of collagen exhibits, according to the work reported, features characteristic of crystal-liquid transitions in other polymeric substances—a well defined melting temp. which is determined only by the composition of the collagen-diluent mixture and is independent of the previous thermal history of the sample; a time-dependent recrystallisation, suggesting the need for some sort of renucleation to precede cryst. growth, as has been found for polymers generally; and the virtual recovery after recrystallisation of the initial melting temp.

J.W.D.

Polymerisation of Resins in relation to Leather Finishes

H. Naidus, G. Katz, and M. Potash

J. Amer. Leather Chem. Assoc., 51, 6-19 (Jan. 1956)

The use of polymer emulsions to produce leather finishes is discussed; a wide range of variation in film character, gloss, mechanical stability, and adhesion is possible. It is generally more satisfactory to select the correct polymer emulsion than to attempt to modify (by compounding) one that is not altogether suitable.

J.W.D.

Ion-exchange Resins and their Applications in Leather Chemistry (XIV p. 260)

XIII—RUBBER; RESINS; PLASTICS**Freezing-point Curves for Binary Systems of ϵ -Caprolactam with Carboxylic Acids**

P. F. van Velden

Rec. Trav. chim., 75, 58-62 (Jan. 1956)**Melting Range of Semicrystalline Polymers and Copolymers**

M. Dole

J. Polymer Sci., 19, 347-352 (Feb. 1956)

An equation is derived for the weight-average crystallite length of crystallisable sequences between non-crystallising copolymer units. The equation is used to estimate the depression of m.p. due to the subdivision of the crystalline regions into small crystallites. An explanation is given for the failure of the value of the heat of fusion calculated from f.p. lowering to agree with observed values.

W.R.M.

Viscoelastic Properties of Polyethylene

E. Catsiff, J. Offenbach, and A. V. Tobolsky

J. Colloid Sci., 11, 48-50 (Feb. 1956)

The transition region between rubbery and glassy modulus is spread over a wider temperature range than for amorphous polymers. Modulus values decrease with increasing temperature, especially near the m.p., because of the relatively large decrease in crystallinity as the m.p. is approached. X-Ray determinations of scattering intensity of stretched samples indicate approximate constancy with time of crystallinity and orientation. Birefringence and X-ray results indicate a marked decrease in crystallinity and orientation as the temperature is raised, particularly near the m.p. Time effects seem to be small.

W.R.M.

Dimorphism of Polyglycine

A. B. Meggy and J. Sikorski

Nature, 177, 326-327 (18 Feb. 1956)

Electron-microscope studies of polyglycine II show crystals which are almost hexagonal in shape. The crystals show growth steps and lattice dislocations. The transition polyglycine I \rightleftharpoons polyglycine II seems to be temperature-dependent. Precipitation of polyglycine I from calcium chloride solution at 100°C. gives polyglycine I. At temperatures between 60° and 100°C. an intermediate X-ray pattern is obtained, but type II is obtained below 60°C. The density of polyglycine increases with increasing degree of polymerisation.

W.R.M.

Cyclic Polyamides from 6- and 6,6-Nylon Polymers

P. H. Hermans; C. J. Brown, A. Hill, and P. V. Youle; and M. A. T. Rogers

Nature, 177, 126-129 (21 Jan. 1956)

Cyclic oligomers from hydrolysis of ϵ -caprolactam polymerisates are separated and identified by paper chromatography. They are found to be the dimer, trimer, and tetramer. The low reactivity of these in hydrolysis, compared with that of the cyclic diamide from 6,6-nylon, is ascribed to internal hydrogen bonding. Boiling of the 6,6-nylon polymer in water followed by evaporation of the aqueous extract yields two materials. One, soluble in ethyl acetate, is identical with the sublimate obtained by heating the polymer above its m.p. in an inert atmosphere and appears to be cyclic hexamethylene-adipamide monomer. The other appears to be the dimer. Three methods are given for the synthesis of a 14-membered cyclic diamine (1:8-diazacyclotetradecane). Two of these start from 6,6-nylon cyclic monomer and the cyclic dimer from ϵ -caprolactam respectively. The third uses *N*-hydroxyhexamethyleneimine as starting material.

W.R.M.

Mass Spectra of Thermal Degradation Products of Polymers

P. Bradt and F. L. Mohler

Bur. Stand. J. Res., 55, 323-327 (Dec. 1955);*Research Paper 2637*

Polymers are degraded from a tube furnace directly into a mass spectrometer. Mass spectra are recorded as the temperature of the sample is increased. Polyethylene degrades into paraffins, olefins, and diolefins, and at 386°C. products of mass 684, $C_{14}H_{24}$, are obtained. Polyvinyl chloride degrades in two stages, losing HCl and benzene at 127-300°C. and evolving hydrocarbons above 300°C.

The heavy fraction from rubber degradation gives molecules containing 3-16 isoprene units, the heaviest product being $C_{36}H_{52}$. Degradation of polyxylylene gives molecules containing 1-9 monomer units, the heaviest product being $C_{72}H_{112}$. A low polymer of polyphenyl gave molecules containing 2-11 monomer units, the heaviest product being $C_{66}H_{86}$.

W.R.M.

PATENTS

Polyvinyl Chloride-Epoxy Resin Coating Compositions

Vinyl Products

BP 745,060

Epoxy resins adhere very well to fabric, metal, glass and ceramic surfaces. They are compatible with plasticised polyvinyl chloride, and polyvinyl chloride coating compositions in which they are incorporated have improved adhesion to the foregoing surfaces.

C.O.C.

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Société Rhodiacéta

BP 745,206

The tendency of the polymers to yellow is inhibited by incorporating a stannous salt of a carboxylic or inorganic acid before the mass is spun, extruded or moulded.

C.O.C.

Linear Polyesters of Sulphonyldibenzoic Acids (VI p. 254)

Ion-exchange Resins and their Applications in Leather Chemistry (XIV p. 260)

Morphology of Large-chain Molecules (XIV p. 260)

XIV—ANALYSIS; TESTING; APPARATUS**Van Slyke Manometric Apparatus modified for Determination of Free Amino Nitrogen in Solid Samples**

K. T. Williams and M. C. Long

Anal. Chem., 28, 144 (Jan. 1956)

A ground-glass ball-and-socket joint is used to provide a wider opening into the reaction chamber of the conventional Van Slyke apparatus, thus enabling wool and other fibrous or granular materials to be introduced easily. The apparatus is also made more easy to clean.

J.W.D.

Electrochromatographic Separation of Cationic Surface-active Agents

S. Fumasoni, E. Mariani, and G. Torracca

Chem. and Ind., 69-70 (21 Jan. 1956)

Mixtures of octyl-, decyl-, lauryl-, myristyl-, octadecyl-, and cetyl-pyridinium chlorides have been satisfactorily separated by electrochromatography on filter paper, using a potential difference of 1400 v. between stainless-steel electrodes; the best results were obtained using a sodium borate buffer at pH 9, or a mixed phosphate buffer at pH 6. The spots were detected either by spraying with a soln. (0.1%) of Supranol Red BB (BASF) containing ammonia (sp.gr. 0.88) (1%), or by exposing the strips to iodine vapour. Five electrochromatograms are reproduced and discussed. If certain conditions are fulfilled—these are detailed—quant. estimation is possible by scanning the strips with a densitometer; the precision of the method is better than 10% within the range of max. sensitivity, viz. for spots of 100-300 μ g.

J.W.D.

Determination of Cationic Detergents

A. V. Few and R. H. Ottewill

J. Colloid Sci., 11, 34-38 (Feb. 1956)

A method has been developed for determination of cationic detergents in aqueous solution at concn. of ca. 10^{-3} M. The analysis depends on the formation of a complex between detergent and an anionic dye and extraction of the complex into an organic phase in which the dye is insoluble. The intensity of colour in the organic phase is directly proportional to the concn. of detergent. The method is insensitive to wide variations in pH and salt concentration of the detergent solution.

W.R.M.

Colour Reaction of Salicylic Acid and Nitrite with Cupric Ion

A. L. Underwood

Anal. Chem., 28, 41-44 (Jan. 1956)

The Jorisson reaction yields reliable results only if the pH of the soln., the concn. of NO_2^- (I) and salicylate (II), and the duration of heating are controlled. Optimum conditions are detailed, applicable to a Cu concn. range of

2-9 p.p.m., and having a standard deviation of ~ 0.04 p.p.m. at the optimal concn. of 5 p.p.m. Though the study has not been comprehensive, no serious interferences have been observed. Experimental evidence suggests that I and II first combine to yield an unstable chelating agent, of unknown composition, and this forms a stable complex with Cu.

J.W.D.

Investigation of Colour Reaction between p-Dimethylaminobenzaldehyde and Urea or Ureido Acids

R. E. Cline and R. M. Fink

Anal. Chem., 28, 47-52 (Jan. 1956)

There appears to be an equilibrium reaction between $R-NH-CO-NH_2$ and the hydrochloride of p-dimethylaminobenzaldehyde, yielding a Schiff base hydrochloride. Colour development is strongly suppressed by diln., and there is an optimal concn. of HCl. It would be difficult to determine and maintain a set of optimal conditions giving max. sensitivity and reproducibility for routine work.

J.W.D.

Use of Azo Dyes as Reagents in Inorganic Analysis and as Antibacterials—I

R. Das and S. S. G. Sircar

J. Indian Chem. Soc., 32, 679-686 (Oct. 1955)

The complexes formed between 15 azo dyes produced from salicylic acid and 8-hydroxyquinoline (oxine) and 20 metals are described. Some of these may be used as spot tests for the metals. Insol. complexes, suitable for gravimetric analysis, are given by o-nitroaniline \rightarrow salicylic acid and o-aminobenzoic acid \rightarrow salicylic acid with lead, and by p-aminobenzoic acid \rightarrow oxine with lead and zinc. o-Aminobenzoic acid \rightarrow oxine gives soluble complexes with zinc and mercury(II) which are suitable for colorimetric analysis. Cobalt and silver interfere.

A.J.

Assay of Picric Acid by Coulometry at Controlled Potential

L. Meites and T. Meites

Anal. Chem., 28, 103-106 (Jan. 1956)

At an Hg cathode whose potential is kept constant at -0.40 v. (relative to the saturated calomel electrode) the reduction of picric acid from HCl soln. proceeds rapidly and quant. under the correct conditions to 2:4:6-triaminophenol. It is recommended that the current flowing during the electrolysis should be integrated, and considered, in conjunction with a conventional alkalimetric titration, for the assay of picric acid.

J.W.D.

Artificial Food Colourings and their Determination

L. V. Fungairino and R. Wojciech

Anales bromatol. (Madrid), 6, 473-558 (1954);*Chem. Abs.*, 50, 1222 (25 Jan. 1956)

Review of Spanish and other legislation on artificial food colours and of their determination. 111 references.

C.O.C.

Extraction of Dyes used for Colouring Foodstuffs with Quinoline and their Identification by Chromatography on an Alumina Plate

M. Mottier and M. Potterat

Anal. Chim. Acta, 13, 46-56 (1955);*Chem. Abs.*, 50, 1222 (25 Jan. 1956)

A simple, rapid, and efficient method of analysis of dyes in foodstuffs is to dissolve the material under examination in a solvent of weak eluting power and then absorb the fat-soluble dyes directly into alumina. The water-soluble dyes are extracted with quinoline in presence of a buffer. The dyes are separated by chromatography into alumina plates and identified by comparison with pure dyes treated in the same way.

C.O.C.

Paper Chromatography of Colours permitted by the Argentinian Food Code. I—Coal-tar Dyes. I. Bengal Rose

O. A. Valenciano and A. Ibarra

Rev. Assoc. bioquim. argentina, 20, 145-155 (1955)*Chem. Abs.*, 50, 731 (25 Jan. 1956)

Ascending chromatography of Bengal Rose (tetraiododichlorofluorescein) with 65-70% methanol on Whatman No. 1 paper gave an R_f value of 0.82 in 3-4 hr. at 20°C. Schleicher & Schüll No. 595 paper was less suitable. The R_f in 30-70% ethanol was 0.89-0.94 in 6-8 hr., in 50-70% propyl alcohol 0.91-0.97 in 9-11 hr., and in

55–75% isopropyl alcohol 0.94–0.99 in 8–10 hr. Butanol, isobutanol, and amyl alcohol did not elute Rose Bengal. On some chromatograms of Rose Bengal obtained from various sources a second pink, not violet, spot was also seen.

Chronic Toxicity Studies on Food Colours. I—FD&C Yellow No. 3 and No. 4 in Rats

M. G. Allmark, H. C. Grice, and F. C. Lu

J. Pharm. and Pharmacol., **7**, 591–603 (1955)

Polarography of the Monoximes and Dioximes of Benzoquinone, Naphthaquinone, and Anthraquinone

R. M. Elofson and J. G. Atkinson

Canadian J. Chem., **34**, 4–13 (Jan. 1956)

The monoximes and dioximes of 1:4-benzoquinone, 1:4- and 1:2-naphthaquinone, and 9:10-anthraquinone give well defined waves in the pH range 3–14, which are suitable for analytical work. There is evidence that tautomerism occurs, but it is not possible to deduce the structure of the tautomers or which form is reduced. A.J.

Electron Microscopy of Fibres

Institute of Physics

Nature, **177**, 318–320 (18 Feb. 1956)

Report of a conference at Leeds organised by the Electron Microscopy Group of the Institute of Physics. Outlines are given of papers dealing with scanning and reflexion-type electron microscopes, replication techniques, ultra-thin sectioning, studies of disintegrated fibres, hydrocelluloses produced by the action of mineral acids on cotton and wood, and the fine structure of viscose rayon. W.R.M.

Simplified Cross-sectioning Method for Observation of Skin and Core of Rayon

H. Hara, H. Sado, and I. Hashimoto

Text. Research J., **26**, 44–46 (Jan. 1956)

A bundle of filaments is soaked in water and pushed through a hole (0.5 mm. diameter) in a brass slide 0.2 mm. thick. The bundle is cut close to the surface of each side of the slide. A drop of dye soln. is applied, and the excess removed with blotting paper. Excess dye is removed by applying a drop of water and blotting. A drop of glycerol-water or other suitable mountant is applied, and a dry cover-slip placed over the specimen, which is then ready for immediate microscopic examination. The method gives quantitative results in good agreement with those obtained with a more elaborate technique. J.C.F.

Separation of Unstable Oxidation Intermediates of Cysteine

G. Toennies and J. J. Kolb

Nature, **177**, 281–282 (11 Feb. 1956)

Paper chromatograms obtained by developing spots containing cysteine in HCl-H-COOH with phenol-iso-propanol-water and treating with ninhydrin show progressive change with the age of the spot; periods of 0, 2, 4, and 8 days from application of the spot were studied. There is a steady decrease in cysteine (R_f 0.4) and an increase in cystine (R_f 0.1). Intermediate cpd. which pass through a time-max. appear also at R_f 0.16, 0.23, and 0.27. The method is suggested as a basis for the detection and isolation of unstable oxidation products intermediate between -SH and -SO₂H. J.W.D.

Characterisation of Starch and Related Polysaccharides by Differential Thermal Analysis

H. Morita

Anal. Chem., **28**, 64–67 (Jan. 1956)

The temp. and magnitude of the endo- and exo-thermic reactions undergone by starches and related polysaccharides during pyrolysis are characteristic of the substance used. The curves obtained by means of differential thermal analysis of mixtures of the polysaccharide with calcined Al₂O₃ may be used to identify the cpd. The Al₂O₃ does not appear to be completely inert, and when it is absent, thermal peaks above the 275°C. region are either displaced or suppressed; reproducibility of the results is seriously affected also. The Al₂O₃ also enables small samples to be studied—as little as 20 mg. may be analysed without difficulty. Seven sets of thermograms are reproduced and their implications are discussed. J.W.D.

Resistance to Penetration by Water of Fabrics permeable to Air

Textile Institute Tentative Textile Standard No. 37

J. Textile Inst., **47**, p. 32–p. 34 (Jan. 1956)

Report on Inter-laboratory Hydrostatic Head Tests

J. Lord

J. Textile Inst., **47**, p. 35–p. 40 (Jan. 1956)

Hydrostatic head determinations were carried out at eight different laboratories. Four out of five laboratories, using the procedure laid down in *British Standards Handbook* No. 11, obtained similar average values, the range of means of sets of eight specimens being 37.8–39.8 cm. The fifth laboratory obtained a significantly lower level of results, the cause being unknown. It is concluded that the recommended B.S. procedure is capable of giving reproducible results. J.W.B.

Hydrostatic Head Test for Water-repellent Fabrics

J. Lord

J. Textile Inst., **47**, p. 41–p. 61 (Jan. 1956)

A detailed description of this test is given, including a study of the effect of altering arbitrary conditions. J.W.B.

Estimation of Free Formaldehyde in Resin-treated Cotton Fabrics

J. H. Howard

Amer. Dyestuff Rep., **45**, 53, 57 (30 Jan. 1956)

Aldehydes and ketones react stoichiometrically with hydroxylamine hydrochloride to form oximes, and the liberated HCl may be calculated as aldehyde or ketone as desired. Duplicate 2-g. samples of fabric are wetted in 250-ml. breakers with 25-ml. aliquots of 95% alcohol. 50 ml. of water is added, and the breakers are covered and allowed to stand for 20 min. with occasional stirring. The samples are hand-squeezed and re-extracted twice with 25-ml. aliquots, each time hand-squeezing after 5 min. extraction. The extracts are combined and neutralised potentiometrically to pH 7. Hydroxylamine hydrochloride (2 g.) is added (to each lot) and dissolved, and the solutions are allowed to stand for 30 min. They are titrated to pH 3.4 potentiometrically with 0.01N-NaOH; duplicate blanks are run with reagents only.

$$\text{H-CHO (p.p.m.)} = \frac{(T_1 - T_2) \times N \times 0.03 \times 10^4}{\text{Wt. of sample}}$$

(T_1 = sample titration, T_2 = blank, and N = normality of NaOH). J.W.B.

Ion-exchange Resins and their Applications in Leather Chemistry

K. W. Pepper

J. Soc. Leather Trades Chem., **40**, 17–30 (Jan. 1956)

A review of ion-exchange methods and principles. Several industrial, analytical, and research applications are indicated. J.W.D.

Morphology of Large-chain Molecules

C. Sadron

Nature, **177**, 205–208 (4 Feb. 1956)

Morphological parameters connected with size and shape and configurational statistics are discussed, and methods for determining them are considered. Such methods include measurements of osmotic pressure, light scattering, viscosity and double refraction of flow of solutions, and determination of diffusion constant. Some applications of such measurements are considered. W.R.M.

Relation between Wool Felting and Single-fibre Properties

(VI p. 253)

Electrical Charge on Individual Fibres

(VI p. 253)

Spectral Regions of Daylight which cause Fading

(VIII p. 255)

Classification of Direct Dyes by their Dyeing Properties on Viscose Rayon

(VIII p. 255)

**AZONINE
AND
DURANTINE
DYESTUFFS
FOR
COTTON**

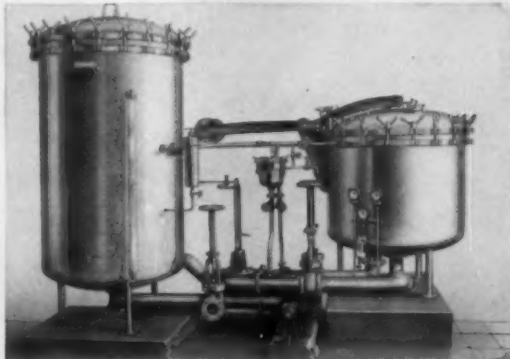


Town End Chemical Works Limited

BRAMLEY LEEDS



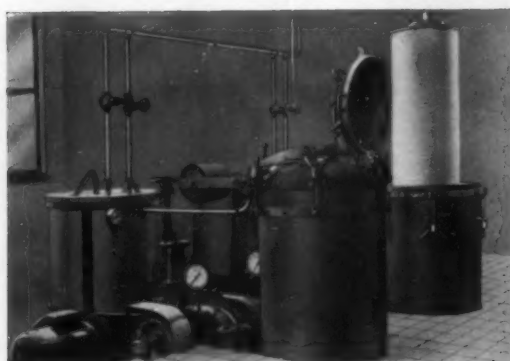
500 lb capacity units for Fast Colour Dyeing Cotton Yarns in Cheese and Cone



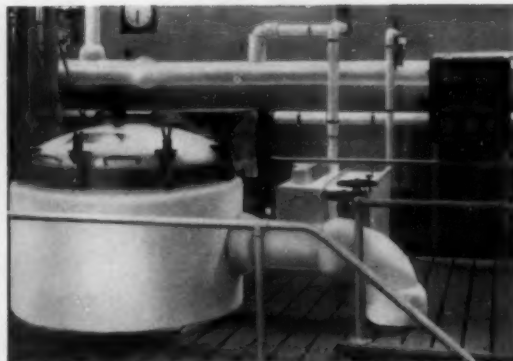
250-300 lb High Temperature Pressure Plant particularly of interest for dyeing synthetics and for Viscose Rayon Cake Dyeing



LONGCLOSE PRESSURE DYEING PLANT



Longclose Pressure Dyeing Plant for Beams — supplied in single and multi-beam units



Rapid Package Drier — available for each size of Longclose Pressure Dyeing Machine

The Longclose range of Pressure Dyeing Plant includes equipment for dyeing Cheeses, Cones, Beams, Ball Warps, Hanks, Viscose Rayon Cakes, Loose Material, Narrow Fabrics, Jute Cops etc., and is in use throughout the world on these many applications.

A wide variety of models and sizes of Pressure Dyeing machines has been developed, enabling the ideal plant to be applied to specific requirements.

Write for details, indicating your requirements, and let us place at your service more than 40 years' experience in this field.



Standard machines available with capacities from 1 lb—1000 lb per batch.

The High Temperature range of Longclose Pressure Dyeing machines allows use of temperatures up to 130°C. — the most efficient system for dyeing the newer synthetic fibres.

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The Publications Committee is prepared to receive Advertisements relating to APPOINTMENTS VACANT, APPOINTMENTS WANTED, or MISCELLANEOUS ITEMS for insertion on this page of the Journal. Advertisements of Appointments Wanted are gratis to individual members, but must not exceed twenty-four words in length.

All inquiries relating to Advertisements in the Journal should be addressed to THE GENERAL SECRETARY, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE.

Replies may be addressed Box —, THE SOCIETY OF DYERS AND COLOURISTS, DEAN HOUSE, 19 PICCADILLY, BRADFORD 1, YORKSHIRE, where all communications relating to these Advertisements are treated in strict confidence.

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A DYING TECHNOLOGIST is required for development and technical service work with a Company in the Midlands. Age is not important provided candidates have had considerable experience in the dyeing and finishing of rayon and synthetic fibres. A good salary will be paid and the appointment is pensionable. Candidates should write giving details of experience and full personal particulars to Box V104.

FOR EMPLOYMENT IN CANADA CHEMISTS FOR FUNDAMENTAL RESEARCH IN CELLULOSE AND RELATED FIELDS

A LARGE RESEARCH ORGANISATION in the vicinity of Montreal serving one of Canada's largest industries requires—
2 PHYSICAL CHEMISTS
2 ORGANIC CHEMISTS

with Ph.D. degree from an accredited university. Previous experience in cellulose research not necessary, but would be an advantage. A thorough training in the fundamentals of chemistry is expected.

Applicants should be male, 23-30 years old and in good health. They should have a pleasant personality, possess initiative and energy, and be willing to accept responsibility.

Laboratories are modern and well equipped; present staff numbers about 150. Starting salary will depend on education and experience. Travelling expenses up to \$350 will be paid.

The Company maintains insurance and retirement plans and offers wide social and recreational facilities, i.e., golf, tennis, skiing, curling, angling, etc.

Apply in writing to Box V98 giving full particulars of education, experience, interests, also attach a photograph.

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A NUMBER of Research Scholarships and Fellowships are available in the Textile Department of the College.

Applicants should communicate with the Principal, Technical College, Bradford 7, for further information and forms of application.

THE UNIVERSITY OF LEEDS

A DEPARTMENT OF COLOUR CHEMISTRY AND DYEING APPLICATIONS are invited for the post of Lecturer in Pigments at a salary on the scale £650-£50 — £1350 a year, according to qualifications and experience. Candidates must have had experience of research in organic, inorganic or physical chemistry, or in an appropriate branch of physics. Experience in the chemistry and technology of pigments is not essential. Applications (three copies) stating date of birth, qualifications and experience, together with the names of three referees, should reach the Registrar, The University, Leeds 2 (from whom further particulars may be obtained) not later than the 1st August 1956.

THE UNIVERSITY OF LEEDS

A APPLICATIONS are invited for the award of the Bradford Dyers Association Ltd. Research Fellowship, tenable in the Department of Colour Chemistry and Dyeing. The Fellowship, which is of the annual value £600-£800, will be awarded for two years in the first instance. It is intended to enable the appointed Research Fellow to carry out studies in dyeing or in chemistry of colouring matters. Applications should reach the Registrar, The University, Leeds 2, not later than 1st August 1956.

CITY OF BRADFORD CONDITIONING HOUSE TEXTILE CHEMIST

A APPLICATIONS are invited for this superannuable post from suitably qualified candidates. The duties involve the chemical testing of textile materials of all types from fibre form to finished products. Candidates should have a sound and extensive practical experience of this type of work which should preferably include ability to deal with the investigation of defective textiles. Preference will be given to candidates holding a University degree or the Associateship of the Royal Institute of Chemistry or other appropriate qualifications. Salary will be in accordance with A.P.T. Division, Grades II-III (£595 to £765 per annum). Commencing salary to be fixed according to qualifications and experience. Applications accompanied by names of two referees and endorsed 'Textile Chemist' should reach me by 9th June 1956.

Town Hall, Bradford 1.

W. H. LEATHEM, Town Clerk

CANADA — Chemist for Dyehouse Laboratory of large textile organisation, specialising in man-made fibres. Age — 35 to 38, preferably married. Must have experience in the analysis of finishes and chemicals, the evaluation of dyestuffs and a sound knowledge of textile chemistry. Good opportunity and prospects. Group Insurance and Superannuation plan in operation. Reply giving full details to Dyehouse Superintendent, Canadian Celanese Limited, Drummondville, Quebec.

DYEING TECHNOLOGIST

COURTAULDS LIMITED require DYEING TECHNOLOGIST for development and technical service work in its Coventry Dyehouse. Previous experience in the dyeing and finishing of rayon and synthetic fibres is essential. Age over 25. The appointment is pensionable.

Candidates should write to the Director of Personnel, Courtaulds Limited, 16 St. Martins-le-Grand, London E.C.1, giving age, experience and any other qualifications. Reference C65 should be quoted when applying.

IMPERIAL CHEMICAL INDUSTRIES LIMITED, Dyestuffs Division, has vacancies in the Dyehouse Department for Technical Officers to assist in technical service, product development and application research covering the industries using the Division's products. An Honours degree (or its equivalent) is required and graduates in organic chemistry, physical chemistry, physics and textile technology can be offered positions of interest and scope with opportunities for travel. Industrial experience may be an advantage, but is not essential. Applications with brief details of experience and qualifications to — Staff Department, Hexagon House, Blackley, Manchester 9.

Important DYERS AND FINISHERS OF TRICOT FABRICS in Switzerland seek absolutely reliable **OVERSEER FOR THE FINISHING DEPARTMENT**. Candidates must have initiative and be capable of developing new ideas of finishing, in co-operation with the management. Persons with practical experience in the field of Cotton, Wool, and Synthetics, circular fabrics and warp looms will be given preference. We offer a good salary, position for life with possibilities of development, and superannuation fund. Offers will be treated confidentially. Offers with photo, curriculum vitae, manuscript test, and salary wanted to cipher 21277 WP. Publicitas, Zurich 1, Switzerland

AGENT required for the sale of auxiliary products to the textile and allied industries. Products consist of albumen fatty acid condensation products, used as dispersing agents for dyestuffs, pigments, etc. Applications invited either from firms or individuals with live and active connections in all branches of the textile and kindred industries

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APPOINTMENTS *continued*APPOINTMENTS VACANT *continued*

JAMES HARDCASTLE & CO. LTD. have vacancies for Chemists in the Research Laboratory, who will also be required to take part in developing processes in the Works. The work is of a very varied and interesting nature, covering bleaching, dyeing, printing and finishing of natural fibres, rayons and man-made fibres.

One appointment would be of a senior nature, and applicants should have a good degree in Chemistry or Colour Chemistry, with several years' post-graduate experience in either printing or dyeing and finishing. They should be familiar with Works practice, and should be capable of planning laboratory investigations and supervising the work of others. The age-limits envisaged are 28-40.

There is also a vacancy of a more junior nature, where the requirements are a good degree in Chemistry or Colour Chemistry, or the equivalent. Recent graduates, either without subsequent experience, or with one or two years' experience (not necessarily in textiles) would be considered.

Both posts carry superannuation scheme benefits.

Apply, giving full details of age, qualifications and experience to the Chief Chemist, James Hardcastle & Co. Ltd., Bradshaw Works, near Bolton, Lancs.

PROGRESSIVE Border firm of Commission Dyers require experienced Foreman to supervise all Piece Processing Depts. Must have thorough knowledge of woollen and worsted piece dyeing; wet and dry finishing; also good organising ability. Pension scheme, low-rent house available. Write, in confidence, giving full details of age, experience and range of salary expected, to Box 4255, Robertson & Scott, 42 Charlotte Square, Edinburgh 2.

REQUIRED by important Egyptian vertical concern producing cotton, viscose and nylon goods. Manager of Dyeing Department who must have considerable technical background and experience in dyeing cotton yarn in circulating machines and cotton pieces on jiggers. Some knowledge of screen printing, dyeing of viscose in yarn and piece, and nylon is expected. Knowledge of French language would be advantage. Good salary and emoluments for right man. Apply giving full details career and marital status in strict confidence to Box V105.

TECHNICAL ASSISTANT of Inter B.Sc. or equivalent for work in Technical Service Laboratory on evaluation of synthetic resin products in textile applications. Preference to applicants with textile experience. The appointment is permanent, pensionable and offers scope for advancement. Applications in writing stating age, qualifications and experience to Vinyl Products Ltd., Butler Hill, Carshalton, Surrey.

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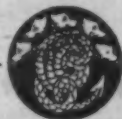
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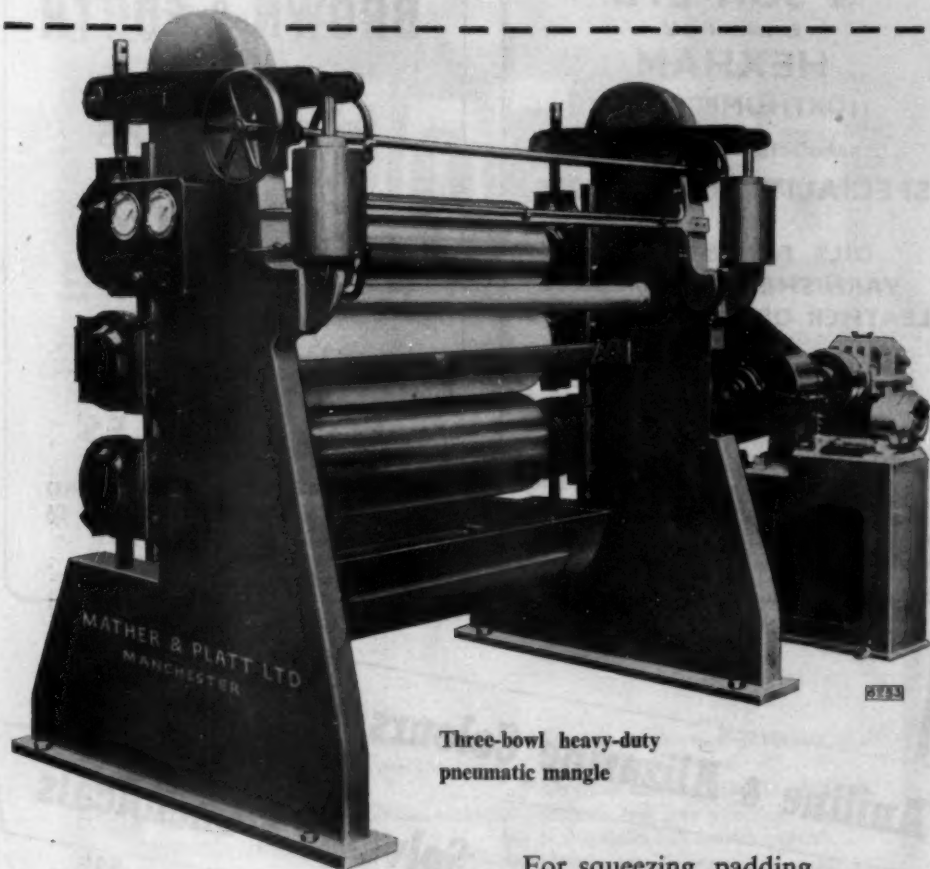
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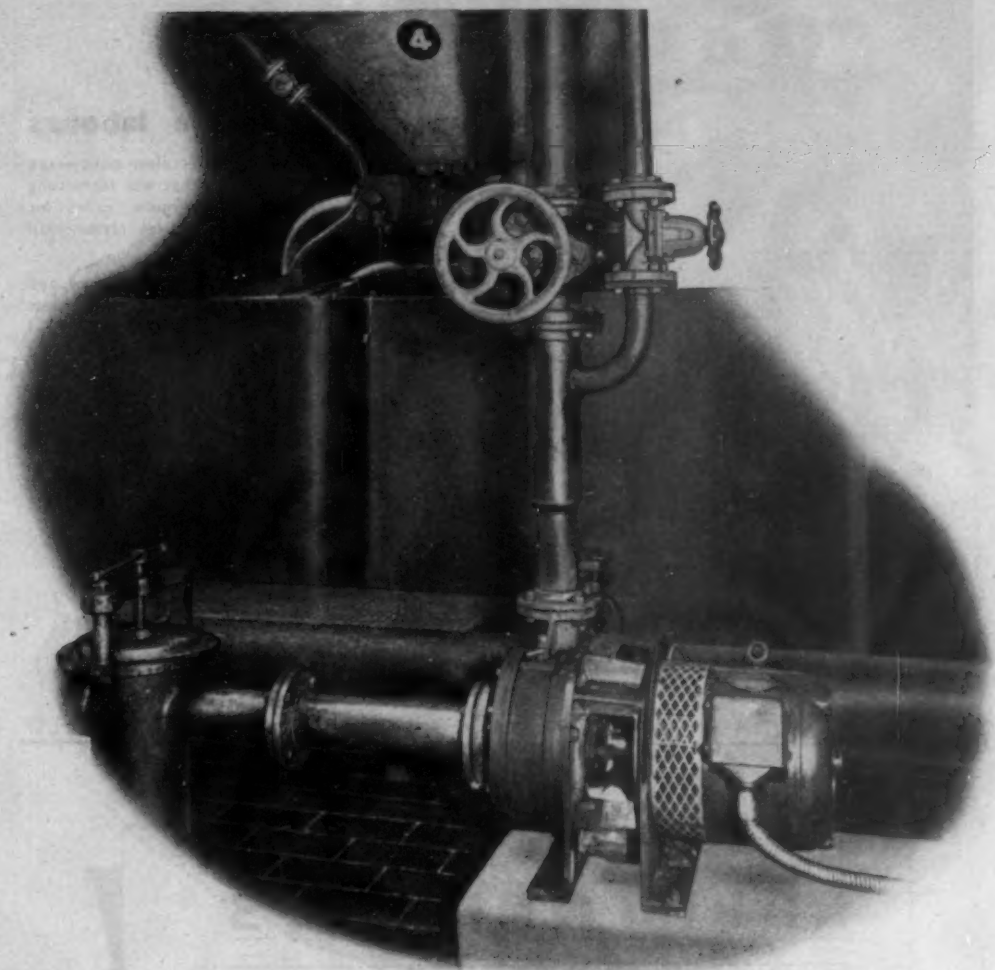
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INDEX TO ADVERTISERS

Page	
vii	Albright & Wilson Ltd
xxvii	Brotherton & Co Ltd
xxxvii	Brown & Forth Ltd
xix	Ciba Ltd
xxiii	Clayton Dyestuffs Co Ltd
xxxvii	Cole & Wilson Ltd
xxxv	Colne Vale Dye & Chemical Co Ltd
xxviii	John Dalglish & Sons Ltd
xv	Drayton Regulator & Instrument Co Ltd
ii	Wm. Edge & Sons Ltd
xii	Norman Evans & Rais Ltd
xxxv	Chas. Forth & Son Ltd
ii	Gardinol Chemical Co Ltd
xvi	Geigy Co Ltd
xvii	Geigy Co Ltd
xxix	Gemec Chemicals Co
xxv	Glovers (Chemicals) Ltd
xxxvi	Hardman & Holden Ltd
iii	Hathernware Ltd
xxi	Hexoran Co Ltd
xiii	L B Holliday & Co Ltd
iv	Hunt & Moscrop Ltd
x	Imperial Chemical Industries Ltd
xxiv	Imperial Chemical Industries Ltd
iii	Laporte Chemicals Ltd
xxii	John W Leitch & Co Ltd
xxxii	Longclose Engineering Co Ltd
xxxviii	Mather & Platt Ltd
i	Newell (Chemicals) Ltd
xiv	Samuel Pegg & Son Ltd
xxxvii	L J Pointing & Son Ltd
xxvi	James Robinson & Co Ltd
vi	Royal Institute of Chemistry
ix	Sandoz Products Ltd
xi	Sandoz Products Ltd
xxxix	Saunders Valve Co Ltd
xi	T Saville Whittle Ltd
v	Shell Chemical Co Ltd
i	Shirley Developments Ltd
xx	F Smith & Co (Whitworth) Ltd
vi	Standard Chemical Co
xi	Staveley Iron & Chemical Co Ltd
xxx	Tennants Textile Colours Ltd
viii	W P Thompson & Co
xxxi	Town End Chemical Works Ltd
vi	Tragasol Products Ltd
ii	J B Wilkinson (Chemicals) Ltd
xviii	Yorkshire Dyeware & Chemical Co Ltd

